Single-Pulse Shock Tube Studies of the Decomposition of Ethoxy Compounds

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Received: February 24, 1997; In Final Form: May 16, 1997[⊗]

Tetraethyl orthocarbonate (TEOC), diethyl carbonate (DEC), and diethoxymethane (DEM) have been decomposed in single-pulse shock tube experiments. TEOC decomposes to give DEC, ethylene, and ethanol as organic products, while DEC results in only the latter two. In both cases the ethylene to ethanol ratio is equal to 1, and the mechanisms appear to involve molecular eliminations. The rate expressions for the initial processes are the following: $k(\text{TEOC} \rightarrow \text{products}) = 10^{13.91\pm0.14} \exp((-27\,529 \pm 348)\text{K}/T)$ s^{-1}, $T = 1005-1180$ K; $k(\text{DEC} \rightarrow \text{C}_2\text{H}_5\text{OCO}_2\text{H} + \text{C}_2\text{H}_4) = 10^{13.03\pm0.11} \exp((-23\,290 \pm 26\,7\,\text{K}/T))$ s^{-1}, $T = 955-1095$ K. The listed uncertainties are one standard deviation. DEM decomposes more slowly than the other two compounds. For each DEM reacted, 1.2 ethylene and 0.5 ethanol are produced. Methane and ethane are also observed as products. The mechanism is postulated to involve both molecular and bond-breaking channels. It is concluded that ethanol arises only through the molecular channel, and on this basis the following rate expressions have been derived: $k(\text{DEM} \rightarrow \text{products}) = 10^{15.93\pm0.15} \exp((-36\,179 \pm 403\,\text{K}/T))$ s^{-1}, $T = 1150-1260$ K; $k(\text{DEM} \rightarrow \text{ethanol} + \text{products}) = 10^{15.07\pm0.45} \exp((-34\,517 \pm 1090\,\text{K}/T))$ s^{-1}; $k(\text{DEM} \rightarrow \text{ethyl} + \text{OCH}_2\text{OC}_2\text{H}_5) = 10^{16.32\pm0.45} \exp((-38\,214 \pm 1160\,\text{K}/T))$ s^{-1}. The results are compared with those dealing with the stability of analogous ethers, esters, and silicon compounds. For carbon compounds the addition of ethoxy groups to the compound destabilizes the molecule. It is further concluded that rate data on the molecular decompositions of ethoxy carbon compounds cannot be easily extrapolated to silicon-containing species.

Introduction

This paper deals with the thermal stability of organic compounds containing adjacent ethoxy groups. Three compounds, tetraethyl orthocarbonate (TEOC), diethyl carbonate (DEC), and diethoxymethane (DEM) have been selected for study. Earlier work[1−11] has shown that the primary pathway for the decomposition of organic compounds containing ethoxy or other larger alkoxy groups is through molecular reactions leading directly to stable compounds. Currently, except through analogies, there is no basis for predicting the decomposition rate expressions of such processes. Thus the thermal stability characteristics of such compounds are very uncertain. This is in contrast to the situation for bond-breaking reactions where fairly good estimates can be made from the thermochemistry.

Table 1 contains a summary of earlier work on a number of compounds that have similarities to those being studied here or are used in the analysis of the data. The general decomposition mechanisms are illustrated in Figure 1. Much work has been done to establish the decomposition mechanism of the carbonates (see e.g. ref 4 and citations therein). It is now generally accepted that for carbonates containing a β hydrogen the only important initial process is a six-center retro-ene reaction (Figure 1a). Likewise alcohols and ethers are well known to undergo a four-center 1,2-elimination to generate an alkene and either water or the respective alcohol (Figure 1b). We are unaware of any previous work on the decomposition mechanisms of diethoxy or tetraethoxy compounds. It is noteworthy that six-center processes involving the transfer of hydrogen have only been firmly established in cases where the starting material contains a π-bond. Also included in Figure 1 is a six-center transition state for the instance where there is no double bond in the parent compound. This type of reaction has less precedent but has been invoked by Chu and co-workers[12] to explain some aspects of tetraethoxysilane (TEOS) decomposition. Even for TEOS, however, our recent studies[11] suggest that the four-center process is the only important molecular channel.

The reactions of TEOC or DEM have not been studied to our knowledge, but there are three lower temperature studies (550−710 K) on DEC decomposition.[1−3] They all agree that equal amounts of ethylene, ethanol, and carbon dioxide are formed. The rate coefficients of Bigley and Wren[2] are in quite good agreement with those of Cross et al.,[3] whereas the values of Gordon and Norris[1] are about a factor of 5 to 10 higher. The data in Table 1 show that DEC and ethyl methyl carbonate decompose much faster than ethyl acetate, which indicates that the substitution of the methyl group by an additional ethoxy or methoxy destabilizes the molecule by an appreciable factor. In contrast, methoxy for ethoxy substitution leads to rate constants that are roughly a factor of 2 smaller. Since this is about equal to the change in the reaction degeneracy, the nature of the nonreacting alkoxy group seems to have little effect on the rate constant. All of the results are consistent with the usual[4] assumption that the initial product is a hydroxy−alkoxy compound which rapidly decomposes to form the alcohol.

Figure 2 contains some relevant bond dissociation energies (BDEs) for DEM,[13,14] where we adopt the usual convention that the BDE is equal to the enthalpy of reaction at 300 K. Values for the stronger bonds should be fairly accurate since they are based on either known values of the radicals and parent compounds or the assumption that γ-substitution of O for CH$_2$ should have minimal effect on the relevant bond energies. To derive a value for the weakest bond, the enthalpy of formation of the OCH$_2$OC$_2$H$_5$ radical needs to be known. We are unaware of any experimental enthalpy values for this type of radical and have assumed that the O-atom substitution for methylene at the β-position will have negligible effects. This may be subject to some error.
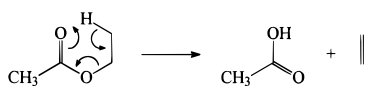
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TABLE 1: Rate Expressions for Some Decomposition Processes Relevant to the Present Study

| substance reaction	rate expression (s^{-1}), temp (K)	ref
diethyl carbonate	7.9×10^{13} exp($-23\ 154$ K/T), 573$-$647	1
$(C_2H_5O)_2C{=}O \rightarrow C_2H_4 + C_2H_5OCO_2H$	1.6×10^{13} exp($-23\ 350$ K/T), 554$-$594	2
	4.0×10^{13} exp($-23\ 750$ K/T), 663$-$708	2
	1.1×10^{13} exp($-23\ 454$ K/T), 584$-$683	3
	1.1×10^{13} exp($-23\ 290$ K/T), 955$-$1095	TW[a]
ethyl methyl carbonate	5.0×10^{13} exp($-23\ 154$ K/T), 573$-$647	1
$C_2H_5OC(O)OCH_3 \rightarrow C_2H_4 + CH_3OCO_2H$	5.2×10^{11} exp($-21\ 890$ K/T), 582$-$667	3
	1.6×10^{12} exp($-22\ 545$ K/T), 626$-$682	4
ethyl acetate	4.0×10^{12} exp($-24\ 155$ K/T), 772$-$1156	5,6
$CH_3CO_2C_2H_5 \rightarrow C_2H_4 + CH_3CO_2H$		
diethyl ether	1.0×10^{13} exp($-31\ 300$ K/T), 753$-$798	7
$C_2H_5OC_2H_5 \rightarrow C_2H_4 + C_2H_5OH$	8.0×10^{13} exp($-33\ 230$ K/T), 783$-$823	8
t-butanol	7.8×10^{14} exp($-33\ 162$ K/T), 1025$-$1200	9
t-$C_4H_9OH \rightarrow i$-$C_4H_8 + H_2O$	4.0×10^{14} exp($-33\ 300$ K/T), 920$-$1175	10
tetraethoxysilane	2.0×10^{15} exp($-34\ 900$ K/T), 1164$-$1278	11
$(C_2H_5O)_4Si \rightarrow C_2H_4 + (C_2H_5O)_3SiOH$		

[a] This work.

(a) Retro-ene reaction

(b) 1,2-Elimination
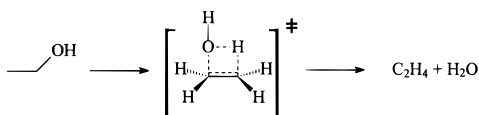
(c) Six-center elimination (possible, but not well-established)
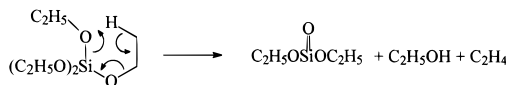
Figure 1. Some possible concerted processes in the decomposition of ethoxy compounds: (a) retro-ene decomposition of ethyl acetate, (b) 1,2-elimination of water from ethanol, and (c) six-center elimination as suggested by Chu et al.,[12] for TEOS decomposition.
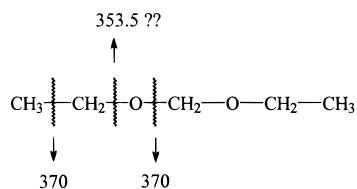
Figure 2. Estimated bond dissociation energies for DEM in kJ/mol.

The enthalpies of reaction at 300 K (BDE) need not be equal to the measured activation energies for bond breaking as determined from experiments near 1100 K. Experience with alkanes indicates that if the BDE values are indeed correct, the actual experimental activation energies can be as much as 20 kJ/mol lower.[15] This is due to the relation between enthalpy and activation energy $\Delta H = \Delta E + RT$ (assuming no activation energy for the reverse combination process) and the temperature dependence of the bond energy due to heat capacity effects. Although the activation energies for bond cleavage reactions are large, the high A-factors for bond-breaking reactions (in the $10^{16}-10^{17}$ s^{-1} range) can make such processes competitive with the molecular channels at the high temperatures used in these shock tube experiments.

Cleavage of the weakest bond in DEM (Figure 2) leads to ethyl and the $OCH_2OC_2H_5$ radical. Both species can readily decompose through low-energy β-fission reactions. A key

mechanistic consequence is that it will be impossible to form ethanol from these or any of the other radical fragments (CH_3CH_2O, CH_2OH, etc.) that may be decomposition products in these shock tube experiments. This is because the only straightforward way of forming ethanol from a radical fragment would involve a radical recombination. At the high temperatures and low radical concentrations of our experiments such bimolecular reactions cannot possibly compete with the facile unimolecular decompositions of the radicals.
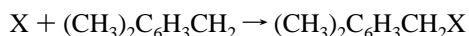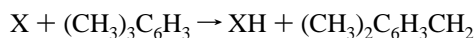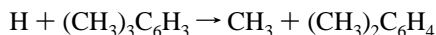
Recently, there has been considerable interest in the decomposition of TEOS[11] since it is widely used in the semiconductor industry for the chemical vapor deposition of silicon dioxide and a report on its mechanism of decomposition has appeared.[6] The present study will yield some interesting information on the effect of silicon for carbon substitution. In view of the increasing interest in silicon compounds for materials synthesis and processing applications and the large volume of existing data on the thermal decomposition of organic compounds, such information may prove to be extremely useful. It should also be noted that many chemical agents contain alkoxy groups attached to phosphorus. The destruction of such compounds is currently an important issue. Here again the thermal stability characteristics are very important.

The single-pulse shock tube method which was used in this study is a very suitable technique for determining the mechanisms and rate constants for the decomposition of large organic molecules. The short reaction time assures that surface processes cannot occur and radical chain reactions can be completely eliminated through the use of large quantities of an inhibitor. The use of gas chromatography allows us to work with dilute concentrations, thus eliminating bimolecular reactions and allowing us to isolate the primary unimolecular processes. True thermal unimolecular rate constants are being measured. The use of an internal standard to determine the reaction temperature leads to the determination of precise rate constants and expressions, since these values are now constrained primarily by the accuracy of concentration determinations by gas chromatography (GC).

Experimental Section[16]

Our experiments were carried out in a heated single-pulse shock tube designed to permit us to study relatively nonvolatile compounds. The shock tube and the associated gas handling and preparation system were all maintained at 108 °C. Analysis of the reactants and products was by gas chromatography. The heavier components were determined using a 530 μm i.d. 30 m carbowax capillary column in the programmed temperature

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mode, while the lighter species were analyzed on a 2 m × 1 mm i.d. HayeSep S column followed by a 1 m × 1 mm i.d. column packed with HayeSep N. Mesitylene (1,3,5-trimethyl-benzene) was used as the chemical inhibitor. It is thermally stable under our conditions and inhibits chain processes through the reactions:

$$H + (CH_3)_3C_6H_3 \rightarrow CH_3 + (CH_3)_2C_6H_4$$

$$X + (CH_3)_3C_6H_3 \rightarrow XH + (CH_3)_2C_6H_3CH_2$$

$$X + (CH_3)_2C_6H_3CH_2 \rightarrow (CH_3)_2C_6H_3CH_2X$$

The substituted benzyl radicals produced by hydrogen abstraction are thermally stable under the present reaction conditions. Their resonance stabilization renders them highly unreactive to stable species. They have few options other than radical recombination reactions, thus rapidly terminating any chain processes.

Standard Reactions. As internal temperature standards we used the well-known decompositions of ethyl acetate to ethylene and acetic acid, of 2-chloropropane to propylene and HCl, and of *t*-butanol to isobutene and water. Ideally a single temperature standard would be used, but the choices were dictated both by the temperature ranges of the decompositions and the necessity of separating the components in the GC analyses. To best compare the relative rates it is obviously desirable to use a self-consistent set of rate coefficients for the standard reactions. In the case of TEOC and DEC it is therefore necessary to establish the relative rates of the ethyl acetate and 2-chloropropane decompositions. This was accomplished by using the absolute rate parameters for the ethyl acetate decomposition from ref 5 and then using the measured relative rates *k*(ethyl acetate)/*k*(2-bromopropane)[17] and *k*(2-bromopropane)/*k*(2-chloropropane)[18] to establish a consistent value for 2-chloropropane. This leads to a slightly larger rate constant than originally[19] reported for 2-chloropropane, but is consistent with other relative rate studies from this laboratory.[15] The adopted rate parameters are

$$k(\text{ethyl acetate} \rightarrow CH_3CO_2H + C_2H_4) =$$
$$4.0 \times 10^{12} \exp(-24\ 155K/T) \text{ s}^{-1}$$

$$k(\text{2-chloropropane} \rightarrow \text{propylene} + HCl) =$$
$$5.2 \times 10^{13} \exp(-25\ 413K/T) \text{ s}^{-1}$$

The above compounds decompose too rapidly to serve as effective standards for DEM, which reacted much more slowly than TEOC or DEC. In the experiments with DEM, *t*-butanol was selected as the standard. The rate parameters $k(t\text{-butanol} \rightarrow \text{isobutene} + H_2O) = 6.0 \times 10^{14} \exp(-33\ 640 \text{ K}/T)$ were chosen as discussed in ref 11. At the higher temperatures of our study, a second channel, $t\text{-butanol} \rightarrow CH_3 + (CH_3)_2COH \rightarrow \text{acetone} + H + CH_3$, becomes important enough that it must be taken into account. From the measured *t*-butanol, isobutene, and acetone concentrations, the average reaction temperature can be calculated by the relation

$$\ln([t\text{-butanol}]_i/[t\text{-butanol}]_f) = \tau(1 + [\text{acetone}]_f/[\text{isobutene}]_f)$$
$$(6.0 \times 10^{14} \exp(-33\ 640 \text{ K}/T))$$

where the subscripts i and f refer to initial and final concentrations, τ is the residence time of 500 μs, T is the reaction temperature, and the rate expression is that for the isobutene channel.

Chemicals. The 2-chloropropane, *t*-butanol, mesitylene, tetraethyl orthocarbonate, and diethyl carbonate were purchased

TABLE 2: Mixtures Used in the Present Study[a]

substrate	standard	inhibitor
340 ppm TEOC	410 ppm ethyl acetate	1% 135TMB[b]
410 ppm DEC	410 ppm 2-chloropropane	1% 135TMB
250 ppm DEM	125 ppm *t*-butanol	1% 135TMB

[a] Argon was the diluent for all mixtures. [b] 135TMB = 1,3,5-trimethylbenzene.

from Aldrich and 4-methylcyclohexene was from Wiley Organics. Except for vigorous degassing and removing of ethanol from the ethoxy compounds by the use of 0.2 nm molecular sieves, they have been used without further purification. The argon from Matheson was of Ultrapure Grade.

Results

The mixtures used in these studies are given in Table 2. The reaction pressures ranged from 200 to 400 kPa (2−4 bar). No pressure effect was observed for any of the compounds. For two of the three substrates, TEOC and DEC, the decomposition processes are very clean in the sense that they yield a few specific products, and excellent mass balances could be achieved. Both TEOC and DEC lead to the formation of equal amounts of ethylene and ethanol, while TEOC produces DEC as an additional product. The net molar yield of DEC per reacted TEOC ranged from 0.68 at the lowest temperature to 0.03 at the highest. At all temperatures the sum of DEC, ethanol, and ethylene accounted for the total reacted TEOC. These observations make it apparent the mechanism involves the process TEOC $\rightarrow$ DEC + C$_2$H$_4$ + C$_2$H$_5$OH, followed by decomposition of DEC. While the overall reaction seems clear, it is uncertain if DEC is formed directly from TEOC in a single step (e.g. Figure 1C) or whether there is a very unstable triethoxycarbinol intermediate:

$$TEOC \rightarrow C_2H_4 + (C_2H_5O)_3COH$$

$$(C_2H_5O)_3COH \rightarrow DEC + C_2H_5OH \quad (\text{fast})$$
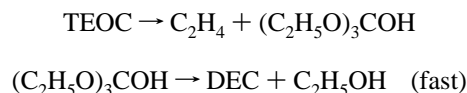
In the case of DEC our data support previous[1−3] suggestions that the overall process is DEC $\rightarrow$ CO$_2$ + C$_2$H$_4$ + C$_2$H$_5$OH. As indicated in the Introduction, the reaction is believed[4] to proceed in two steps, a retro-ene reaction followed by rapid decomposition of the alkoxy acid:

$$DEC \rightarrow C_2H_4 + C_2H_5OCO_2H$$

$$C_2H_5OCO_2H \rightarrow CO_2 + C_2H_5OH \quad (\text{fast})$$
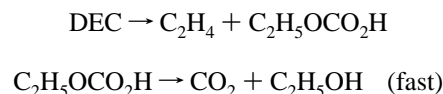
If the alkoxy acid is indeed an intermediate, the 1:1 ratios of ethanol to ethylene establish that it is fully decomposed under our conditions.

Arrhenius plots of the rate constants for decomposition of the TEOC and DEC can be found in Figure 3. Rate constants for DEC can be derived both from the direct studies of this compound and from the TEOC experiments where DEC is an intermediate. The results are in excellent agreement which strongly supports our postulated mechanism for TEOC decomposition.

The rate expressions for the two decomposition processes are

$$k(TEOC \rightarrow \text{products}) =$$
$$10^{13.91\pm0.14} \exp(-27\ 529 + 348 \text{ K}/T) \text{ s}^{-1} \quad (1005-1180 \text{ K})$$

$$k(DEC \rightarrow C_2H_4 + C_2H_5OCO_2H) =$$
$$10^{13.03\pm0.11} \exp(-23\ 290 + 267 \text{ K}/T)\text{s}^{-1} \quad (955-1095 \text{ K})$$

The small uncertainties given above are one standard deviation

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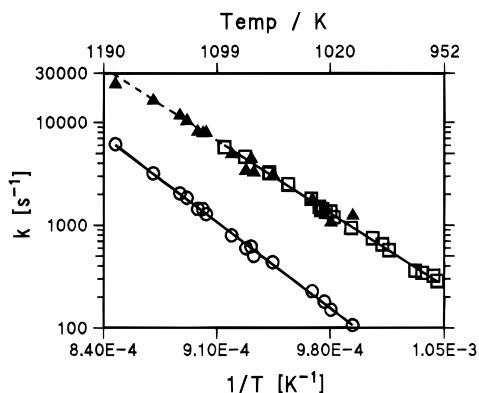*J. Phys. Chem. A, Vol. 101, No. 30, 1997* **5497**

Figure 3. Arrhenius plots for the decomposition of TEOC (○) and DEC (□). Also included in the plot are DEC decomposition rate constants calculated from experiments with TEOC where DEC is an intermediate (▲).

and reflect only the experimental scatter. They do not include possible systematic errors or uncertainties in the rate parameters of the standard reaction. Taking these into account leads to more realistic uncertainties of a factor of 2 in the A-factor, 500 K in the activation energy, and 30% in absolute rate. The self-consistency of these results, in particular the excellent mass balances, is very important for validating the results on DEM, where the situation is not as unambiguous.

DEM decomposed much more slowly than TEOC or DEC and its product spectrum was more complex. It was found that for every DEM destroyed, approximately 1.2 molecules of ethylene and 0.5 molecule of ethanol were formed. The ethylene and ethanol thus account for about 85% percent of the available ethoxy groups. Significant amounts of methane and ethane were also found and account for much of the missing mass. It should be noted that with a flame ionization detector we are unable to detect compounds such as CO_2, CO, and formaldehyde. The ratio of ethylene to ethanol product increased slightly at higher temperatures.

The nonstoichiometric ratio of ethylene to ethanol, as well as the observation of methane and ethane as products, suggests that DEM decomposition is more complex than the decompositions of TEOC and DEC. Probably at least two parallel paths are important. Since the mechanism is uncertain it is necessary to determine decomposition rate constants from the disappearance of starting material rather than from appearance of product. Because at low conversions we are taking the difference of two large numbers, this method is less accurate than that using product formation. However, for TEOC and DEC the results using product formation and destruction of the starting material were essentially the same, which gives us confidence that the procedure is still satisfactory.

The following represents our attempts at determining the relative contributions of the various pathways for DEM. The possible unimolecular destruction modes are molecular reactions and bond fission reactions. Ethylene can be produced via both pathways, so this product cannot be used to follow a specific channel. As indicated in the introduction, ethanol cannot readily arise from radical intermediates, so its formation must be the result of a molecular process. Two molecular mechanisms seem most likely. One possibility is a six-center reaction leading directly to ethanol and ethylene:
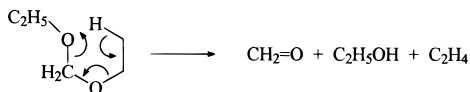
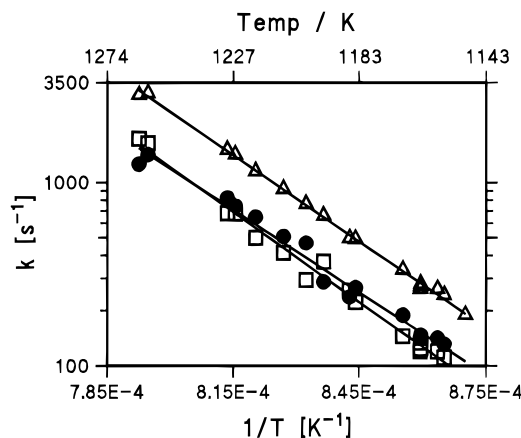An alternative with more precedent is a sequential process where

Figure 4. Arrhenius plots for the overall decomposition of DEM (△), the process that leads to the production of ethanol (●), and the difference between rate constants for DEM destruction and ethanol formation (□), interpreted in terms of bond breaking.

the initial reaction is a four-center elimination of ethylene, and is followed by the rapid elimination of ethanol from the ethoxy carbinol:

$$DEM \rightarrow C_2H_4 + C_2H_5OCH_2OH$$

$$C_2H_5OCH_2OH \rightarrow C_2H_5OH + CH_2{=}O \quad (fast)$$

Both possibilities lead to the formation of a single ethanol from DEM. As long as any ethoxy carbinol intermediate is fully decomposed, we can use ethanol production as a marker for the molecular channel(s). Subtraction of this rate constant from that for total DEM disappearance leads to a rate constant that we associate with bond breaking. On the basis of Figure 1, fission of the $C_2H_5{-}O$ bond is the most important bond fission channel. The results are shown in Figure 4 and lead to the following rate expressions.

$$k(DEM \rightarrow products) =$$
$$10^{15.93 \pm 0.15} \exp(-36\,179 \pm 403\,K/T)\,s^{-1}$$
$$T = 1150{-}1260\,K$$

$$k(DEM \rightarrow C_2H_4 + C_2H_5OCH_2OH) =$$
$$10^{15.07 \pm 0.45} \exp((-34\,517 \pm 1090)K/T)\,s^{-1}$$

$$k(DEM \rightarrow C_2H_5 + OCH_2OC_2H_5) =$$
$$10^{16.32 \pm 0.45} \exp((-38\,214 \pm 1160)K)/T]\,s^{-1}$$

In the above we have postulated the molecular channel that ultimately leads to ethanol to be a four-center process, but it should be realized that the only basis for this assignment is by analogy with more established systems. The quoted uncertainties in our rate expressions are one standard deviation. For the overall process, the total uncertainty is similar to those of the other compounds, about a factor of 2 in the A-factor, 500 K in the activation energy, and 30% in absolute rate. A meaningful estimate of the uncertainties for the rate parameters of the specific channels is more difficult to make since this aspect depends heavily on the correctness of our mechanistic assumptions. In particular is the assumption that the yield of ethanol from the initial molecular channel is 100% over the entire temperature range. At higher temperatures the mass balance can be used as a check, but at low temperatures we are dealing with differences of large numbers and small inconsistencies would be difficult to detect. An error of about 10% at the low end of our temperature range would reduce the A-factor for the
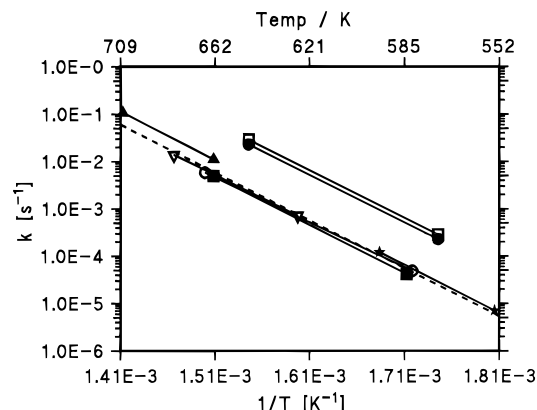
Figure 5. Literature rate constants for the decompositions of DEC and ethyl methyl carbonate. For easier comparison with DEC, the rate constants for ethyl methyl carbonate have been multiplied by a factor of 2 to adjust for the reaction degeneracy. Results for DEC: ●, ref 1; ▲ and ★, ref 2; ■, ref 3; dashed line, extrapolated results from the present work. Results for ethyl methyl carbonate: □, ref 1; ○, ref 3; ▽, ref 4.

molecular channel by about a factor of 3 and decrease the activation energy by about 10 kJ/mol. Conversely, for the bond fission channel the A-factor would be increased by about a factor of 5 and the activation energy by nearly 20 kJ/mol.

Discussion

Decompositions of TEOC and DEC. The clean product spectrum and excellent mass balances found in the decompositions of TEOC and DEC indicate that these processes are molecular in nature. For both substrates we noted the absence of significant quantities of methane, ethane, and the xylenes. The latter is the expected product from H-atom attack on the inhibitor mesitylene, while the first two compounds can arise from methyl radicals that are formed. Clearly, bond breaking, which would inevitably lead to the formation of such radicals, cannot be of any consequence. This deduction is further confirmed by the finding of pre-exponential factors in the range of 10^{13} s^{-1}. Bond fission processes would be expected to yield much larger A-factors in the 10^{16}–10^{17} s^{-1} range. A comparison of our results for DEC with literature data can be found in Figure 5. It can be seen that extrapolation of our results by 5 orders of magnitude lands us among the results of three earlier works.

Nevertheless, our data do not permit us to differentiate between a number of the possible concerted mechanisms. While the mechanism for DEC decomposition seems well-established to be the retro-ene reaction, the situation for TEOC is less clear. An interesting question is whether TEOC decomposes in a six-center process resulting in the simultaneous release of ethylene and ethanol or if the mechanism involves 1,2-elimination of ethylene followed by rapid decomposition of the triethoxy-carbinol to give ethanol. In the absence of a π bond, we are unaware of any well-established precedent for a six-center complex fission involving the transfer of an H-atom. While there are a few molecular decompositions, e.g. 1,3,5-trioxane → 3 H$_2$C=O,[20] which apparently proceed via a six-center transition state in the absence of a π bond, no atoms are transferred and such reactions appear to be substantially different from those considered here. In this respect the 1,2-process seems more likely for the TEOC system. If this is the case, the very satisfactory material balances and 1:1 ratios of ethylene to ethanol demonstrate that the ethoxy carbinol is extremely unstable under our conditions.

Decomposition of DEM. The rate expressions for the two channels in DEM decomposition are subject to the caveat that
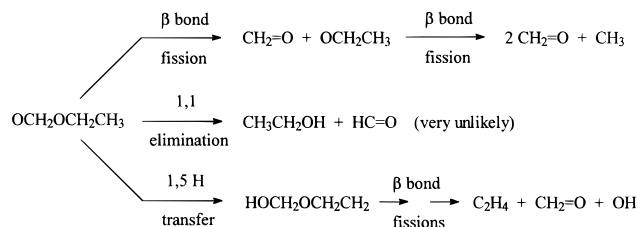

Figure 6. Possible decomposition pathways for the oxygen-containing radical formed by fission of the weakest bond in DEM.

they are dependent on the postulated mechanism. In this regard the A-factor for the molecular channel is larger than expected when compared with the decompositions of TEOC, DEC, or the more similar diethyl ether. One possible scenario is that the initial molecular channel is indeed a 1,2-molecular elimination to form ethylene and ethoxy carbinol, but that this latter compound is not fully decomposed at the lower end of our temperature range. While our mass balance is such that very little of the carbinol could be unreacted, the data are subject to the greatest uncertainty at the lowest extents of reaction. If even 10% of the ethoxy carbinol remained at the lowest temperatures of our experiments, the activation energy for the molecular channel would be reduced by about 10 kJ/mol and the A-factor would be more in line with expectations. Such an explanation would of course imply that the particular carbinol formed from DEM is more stable than those inferred in the decompositions of DEC and TEOC. The likelihood of this is difficult to judge given the complete absence of quantitative data on the decompositions of carbinols.

The derived activation energy for bond breaking in DEM (317 kJ/mol) is much lower than that we have estimated (Figure 2), assuming that β-substitution of O for methylene has no effects. While the A-factor is at the lower end of the range that one would expect for bond breaking, it is close enough that our postulated mechanism appears to be correct. As noted earlier, the weakest bond in DEM is the ethyl−O bond, and the rate parameters should be associated with this bond. Taken at face value, the data indicate that substitution of an oxygen for a methylene group β to the bond being broken decreases the bond energy by about 20 kJ/mol. However, since the rate parameters for this channel were derived by difference, it should be emphasized that this value is strongly dependent on our assumption that the ethoxy carbinol is fully decomposed. An error of about 10% in the rate constant for the molecular channel at the lowest temperatures of our study would increase the A-factor for bond breaking to about 1×10^{17} and lead to an activation energy of about 335 kJ/mol. Because of this, the derived bond energy should be treated with caution.

Cleavage of the weakest bond in DEM (Figure 2) leads to ethyl and the OCH$_2$OC$_2$H$_5$ radical. Ethyl can be expected to decompose to ethylene through fission of a β C−H bond. Possible pathways for the breakdown of the oxygenated radical can be found in Figure 6. Although experimental data do not exist, three channels are possible. The one involving β C−O bond fission is energetically reasonable and is consistent with known pathways in analogous compounds. It leads to formation of formaldehyde and methyl radical. One could conceivably imagine the formation of ethanol through a 1,1 elimination from the OCH$_2$OC$_2$H$_5$ radical. There is, however, no precedent for such a process, and one would expect it to have a barrier substantially higher than that for β C−O bond fission. The third path involves isomerization of the initial radical to HOCH$_2$-OCH$_2$CH$_2$ prior to decomposition. In larger alkyl radicals, such 1,5 processes can be important although relatively few rate data exist. Because HOCH$_2$OCH$_2$CH$_2$ will break down to ethylene,

Decomposition of Ethoxy Compounds

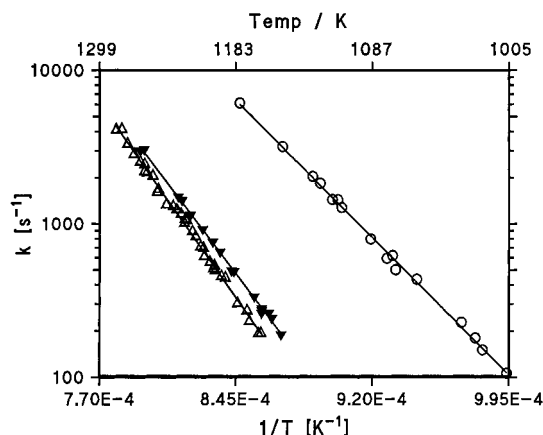*J. Phys. Chem. A, Vol. 101, No. 30, 1997* **5499**

Figure 7. Comparison of present results on DEM (▼) and TEOC (○) with data on TEOS (△).

formaldehyde, and OH, this has an important consequence since it results in two ethylenes (one each from ethyl and HOCH$_2$-OCH$_2$CH$_2$) from bond fission in DEM rather than one if isomerization is unimportant.

On the basis of our product spectrum and postulated mechanism we are able to draw some conclusions as to the fate of OCH$_2$OC$_2$H$_5$. Our data show that for every DEM destroyed, approximately 1.2 molecules of ethylene and 0.5 molecule of ethanol are formed. From the amount of ethanol we can conclude that the molecular channel accounts for about 50% of reaction with the balance presumably due to bond fission. Further, since the molecular channel leads to a 1:1 ratio of alcohol to alkene, the amount of ethylene from the bond fission channel is 1.2 − 0.5 = 0.7 per reacted DEM. Of this amount, 0.5 unit of the ethylene must result from decomposition of the ethyl radical produced in the initial bond fission and the remaining 0.2 from decomposition of OCH$_2$OC$_2$H$_5$. As shown in Figure 6, this can only occur if the OCH$_2$OC$_2$H$_5$ radical undergoes a hydrogen shift prior to β C−O bond fission. Our data indicate that the branching ratio between isomerization and β-bond fission is about 0.4. In a more general sense, the above analysis shows that attempts to model such systems will require that isomerization reactions are properly considered.

Relative Rates of Ethoxy Carbon Compounds. Figure 7 shows that rate constants for TEOC are a factor of 20 to 30 larger than those of DEM in the temperature range under consideration. To compare the rates of the molecular channels, the overall rates should be corrected for the number of ethoxy groups and it should be recalled that for DEM the molecular channel accounted for only about 50% of the overall destruction rate. After these adjustments, the rate difference between what we have postulated as mechanistically similar processes is still a factor of 20−30. This is equivalent to a change in the activation energy by about 33 kJ/mol. If the data on diethyl ether[7,8] are extrapolated to our temperatures, it is seen that the rate constants for the molecular channel vary by more than 2 orders of magnitude and follow the order diethyl ether < DEM < TEOC. It is thus apparent that addition of ethoxy groups to the central carbon atom destabilizes the molecule by an appreciable amount. This is one of the most important

consequences of this study. What is less clear is if the rate differences reflect a relative stabilization of the four-center transition state or if there is an actual change in the mechanism. For instance could the six-center process be important in TEOC, despite the absence of a π system in the parent compound? Resolution of this question must await further studies.

Comparison with Ethoxy Silicon Compounds. TEOS is the silicon analog of TEOC where the central carbon atom has been replaced by silicon. Our results[11] indicate that the molecular elimination reaction of TEOS is a four-center process and, at 1150 K, is a factor of 20 slower than the reaction of TEOC. The derived activation energy for TEOS is nearly 60 kJ/mol higher. It is further interesting that for ethoxy silicon compounds the rate constant for elimination was unaffected by the number of ethoxy groups on the central silicon atom,[11] except for changes associated with the reaction path degeneracy. This contrasts with the carbon compounds where large rate differences are observed. The reasons for the shift in behavior are uncertain. One might speculate that the relative charge-accepting properties of Si and C are important and possibly the large difference in the O−C and O−Si bond lengths. Irrespective of the explanation, it is apparent that rate data from carbon systems are not directly transferable to the silicon compounds. Further, there are presently no methods of predicting the rate constants in lieu of experimental data.

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