do so by this type of mechanism, but in the case of the anisoles and probably the nitrobenzenes rapid isomerization is expected to follow giving the product which would result from rearrangement to the substituted position. Further fragmentation would occur from this substituted ion. The rearrangement to the ortho position therefore constitutes a "hidden" mechanism in high energy ions; this explains why it has not been recognized from the analysis of normal mass spectra.

It may at first sight seem surprising to find a second case of competitive unimolecular eliminations of the same neutral so soon after the anisole study,[1b] but these two systems are rather similar in allowing radical-induced rearrangements to alternative sites on a benzene ring.

This study again highlights the value of the new techniques of detailed analysis of metastable peak shapes and of energy partitioning. It also suggests that correction of mass spectrometric thermochemical data for the presence of a reverse activation energy may soon be feasible. For instance, subtraction of the measured T_1 value from AP($(M - NO)^+$) would much improve the accuracy of a heat of formation value for such an ion obtained by this reaction, and the result could be extrapolated to any aromatic nitro compound. By way of contrast, the correction required in determining the heat of formation of some ion $ArH\cdot^+$ from the appearance potential of the corresponding anisole requires the subtraction of a quantity some six times the T_1 value.

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Kinetics of the Gas-Phase Thermal Unimolecular Elimination of Ketene or 1,1-Dimethylketene from 2,2-Dimethyl-3-ethoxycyclobutan-1-one. A Quasi-Zwitterion Transition State

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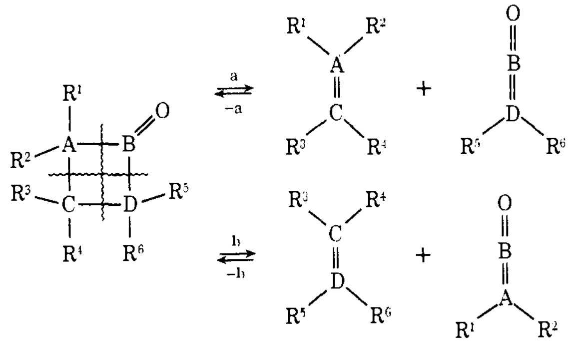
Abstract: The kinetics of the gas-phase thermal decomposition of 2,2-dimethyl-3-ethoxycyclobutan-1-one (DEC) was studied in the temperature range 464–558 K using a static reaction system and gas chromatographic analysis. Two simultaneous concerted pathways yield the product pairs ketene + isobutenyl ethyl ether (65–80% of the total conversion) and 1,1-dimethylketene + vinyl ethyl ether (35–20%). Independent first-order total rate constants for the overall depletion of DEC were calculated based on the internal standard technique (k_{tot}) as well as the amounts of vinyl ethyl ether and isobutenyl ethyl ether observed (k'_{tot}). The rate constants were independent of the initial starting pressure in the range 5–50 Torr and of the total pressure (propylene) of up to 700 Torr and fit the Arrhenius relationships $\log (k_{tot}/\text{sec}^{-1}) = 13.58 \pm 0.29 - (40.27 \pm 0.68 \text{ kcal mol}^{-1})/\theta$ and $\log (k'_{tot}/\text{sec}^{-1}) = 13.61 \pm 0.22 - (40.32 \pm 0.51 \text{ kcal mol}^{-1})/\theta$, where $\theta = 2.303RT$. These activation parameters, when compared with the corresponding values observed for cyclobutanone itself, indicate a stabilizing effect of 3-alkoxy groups of 11.5 kcal mol^{-1}, which is about the same as was observed previously for substituted vinyl groups. The results of this work further substantiate the assumption of an essentially zwitterionic charge separation involved in the gas-phase $2_s + 2_a$ ketene + olefin addition–elimination reactions.

Kinetic studies of the gas-phase thermal elimination of ketenes from cyclobutanone derivatives and particularly the observed substituent effects should yield important information about the detailed nature of the reaction mechanism and the transition state involved in these systems (I), where *A*, *B*, *C*, and *D* represent carbon atoms. In principle, three extreme formulations of the transition-state structures and detailed reaction path may be envisaged: (a) a concerted synchronous process with an essentially symmetrical neutral transition state, (b) a concerted nonsynchronous path involving considerable charge separation and an asymmetric transition state, and (c) a biradical reaction path.



(I)

The first possibility (a) can be ruled out on the basis of the well-known fact that conjugated olefins add to ketenes in a four-center 2 + 2 process to the exclusion of the "allowed" six-center $4_s + 2_s$ Diels–Alder reaction.[1-4] This has been rationalized on the basis of the principle of orbital symmetry conservation, by

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invoking an orthogonal $2_s + 2_a$ transition state and a pseudovinylium ion character of the ketene in the ground state.[5]

With few exceptions,[6] the activation parameters reported to date for the gas-phase elimination of ketenes from cyclobutanone derivatives are incompatible with a biradical analysis.[7] Furthermore, the observed retention of stereochemistry in the olefin moiety[8,9] in the gas-phase elimination process is consistent with a concerted mechanism of the type b.

The polar nature of the reaction is also apparent from liquid-phase studies of the substituent effects on the rates[10,11] and orientations[2,4,12-15] of the addition reaction. The orthogonal structure of the transition-state complex has been demonstrated by studies of the relative rates of elimination of alkyl ketene from 7-*endo*- and 7-*exo*-alkyl substituted bicyclohept-2-en-6-ones.[16]

Earlier studies on the unimolecular gas-phase ketene elimination reactions from bicyclo[3.2.0]hept-2-en-6-one,[17] 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one,[18] and bicyclo[3.2.0]heptan-6-one,[19] carried out in this laboratory, demonstrated that the effective change in charge densities in going from the ground to the transition state occurs essentially on the opposing carbon centers B and C. The polar nature of centers A and D appears to remain effectively unchanged when forming the transition-state structure. These observations are consistent with a quasi-zwitterionic transition state in the gas phase, which would explain the observed large effect ($\sim$12 kcal mol^{-1}) of vinylic substituents on the carbon center C,[17,18] compared to only a relatively small effect ($\sim$3 kcal mol^{-1}) of alkyl substituents.[19]

In contrast, the stabilizing effect of a vinyl group onto the positively induced carbon center in the elimination of hydrogen halide from alkyl halides, considered to be a "model" reaction for a quadrupolar (rather than an essentially dipolar or zwitterionic) type transition state, is with 5.5 ± 0.3 kcal mol^{-1} only 2.7 kcal mol^{-1} larger than was observed for alkyl groups.[20] Methoxy and ethoxy substituents, however, bonded to a positively induced carbon center were observed to exercise a much larger effect than vinyl substituents, lowering the activation energy for HX elimination by more than 20 kcal mol^{-1}.

It was then interesting to measure the effect of a 3-alkoxy group on the rate of elimination of ketene from cyclobutanone in the gas phase, particularly in view of the proposed quasi-zwitterionic transition-state structure.

Experimental Section

(a) Materials. 2,2-Dimethyl-3-ethoxycyclobutanone (DEC) of 99.6% purity was obtained by low-pressure distillation of a sample, prepared by liquid-phase addition of dimethylketene to vinyl ethyl ether and supplied by M. Rey of the Chemistry Department of the University of Zürich. *p*-Ethyltoluene of >99% purity, used as an internal standard (Std) was obtained from Aldrich Chemicals Corp., Inc., Milwaukee, Wis. Five different starting mixtures with ratios of $[DEC]_0/[Std]_0$ of 1.16 ± 0.01, 0.800, 1.00 ± 0.01, 0.911 ± 0.007, and 0.902 ± 0.01 were used. The error limits indicate *maximum* deviations in the ratios of the starting materials observed over a period of several weeks. The mixtures were stored refrigerated under nitrogen pressure.

(b) Apparatus and Procedure. The conventional static reaction system used in these studies has been described in detail earlier.[20] A Teflon-coated stainless-steel reactor of 805-cm^3 volume was used for most experiments. To check for heterogeneity, one of two equivalent cylindrical Pyrex glass vessels of 2060-cm^3 volume was packed with glass tubing resulting in a volume of 1340 cm^3 and a surface to volume ratio 35 times that of the nonpacked reactor.

Liquid samples of the starting material were directly injected into the Teflon reactor *via* a silicone rubber septum or, in the case of the glass vessels, they were injected and evaporated in the heated dead space above the reactors. Pressure changes were observed during the reaction with a pressure transducer.

A reaction was quenched in two ways. (a) For most experiments the reaction products were condensed quantitatively in a trap kept at liquid nitrogen temperature. Noncondensable gases were removed by an automated Toepler pump into a ball buret. Only trace amounts of noncondensable gases could occasionally be detected. The condensed product mixture was distilled into a small vial, containing an appropriate amount of degassed methanol. Upon warming the condensate to room temperature, the primary products ketene and 1,1-dimethylketene reacted with methanol forming methyl acetate and methyl methylpropionate, respectively. This product mixture was then analyzed directly by gas chromatography. (b) In some of the experiments a "light" product fraction, consisting of the two ketenes, ethyl vinyl ether and isobutenyl ethyl ether was quantitatively separated at −20° from the remaining "heavy" product fraction, containing the starting material and internal standard. The "light" fraction was analyzed volumetrically, prior to recondensation into cyclohexanol. After the cyclohexanol solution was warmed to room temperature, the two ethyl ethers (the ketenes reacted with the cyclohexanol) were again transferred *via* the Toepler pump into the ball buret for volumetric measurement. The differences between the two PVT measurements were equated with the amount of ketenes in the reaction products. The ratio of ether/ketene observed in 14 experiments carried out in this manner varied between 1.0 and 2.5, depending on the reaction conditions used, demonstrating a partial loss of ketene during the reaction and the work-up procedures. The "heavy" product fraction was analyzed by gas chromatography.

(c) Analyses. Gas chromatographic analyses were carried out using a F & M Model 810 gas chromatograph fitted with T. C. detectors and a Disc integrator. A 4 m × 0.25 in. column packed with Chromosorb W containing a 33% coating of Carbowax 20M and a helium flow rate of $\sim$100 ml min^{-1} was used. Complete separation of all the reaction products was achieved when the oven temperature was heated from 60 to 165° using a heating rate of 6° min^{-1} and a post injection interval of 15 min. The following retention times in minutes after the air peak were observed: ethyl vinyl ether, 7.5; methyl acetate, 20.4; isobutenyl ethyl ether, 22.7; methanol, 24.5; methyl methylpropionate, 26.8; *p*-ethyltoluene, 41.0; and 2,2-dimethyl-3-ethoxycyclobutan-1-one, 46.0. Response factors were assumed to parallel the molecular weight relationship. The validity of this assumption was demonstrated with observed response factors of 1.36 and 1.35 for vinyl ethyl ether and methyl acetate, respectively, based on *n*-butyl ethyl ether (≡1.00). The corresponding values using the molecular weight relationship are 1.39 and 1.35, respectively. The relative response factor of the

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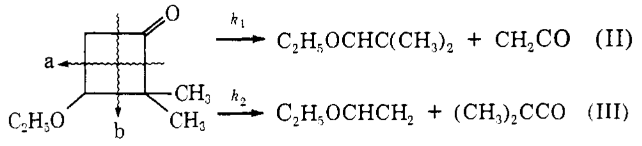
starting material DEC based on the internal standard *p*-ethyltoluene was observed to be 1.02 ± 0.01 compared to 1.18 calculated on the basis of the molecular weight relationship. This is reasonable, considering that oxygenated compounds usually have lower response factors than hydrocarbons on thermal conductivity detectors.

The reaction products vinyl ethyl ether, isobutenyl ethyl ether, methyl acetate, and methyl methylpropionate were unambiguously identified with the nmr spectra of the collected gc eluates.

Results

The gas-phase thermal decomposition of 2,2-dimethyl-3-ethoxycyclobutan-1-one (DEC) was studied in the temperature range 464–558 K. The major primary reaction products are ketene, isobutenyl ethyl ether, 1,1-dimethylketene, and vinyl ethyl ether, whereby the total of these four products always accounted for more than 95% (and in most experiments for more than 99%) of the reaction products, *detected by gas chromatography*.



Depending on the temperature used, the amounts of the product pair ketene + isobutenyl ethyl ether were between two and three times larger than those of 1,1-dimethylketene + vinyl ethyl ether. The only other reaction products (formed in significant but variable quantities) were polymeric materials, detected as a coating of nonvolatile residue accumulated during the course of these studies on the walls of the reaction vessel. The formation of higher molecular weight material, not detected by gas chromatography, was also indicated with pressure changes ranging between 30 and 80% of the amounts calculated on the basis of the actual conversions obtained from gc analyses. Using the concept of direct additivity of thermodynamic increments[7] and recent literature data[21] for the heats of formation of ketene[22] (-11.4 kcal mol^{-1}) and cyclobutanone[23] (-24.20 kcal mol^{-1}), the equilibrium constants $K_{1,-1} = k_1/k_{-1}$ and $K_{2,-2} = k_2/k_{-2}$ for the reaction systems II and III have been calculated for a mean temperature of 500 K to $\log (K_{1,-1}/\text{atm}) \approx \log (K_{2,-2}/\text{atm}) = 9.2 - 19.0/\theta$, where $\theta \approx 2.303RT$. For the lowest reaction temperature of 465 K the equilibrium constant $K_{1,-1}$ equals 10^3 Torr (throughout this paper, 1 Torr = (101.325/760) kN m^{-2}). In calculating k_1 and k_2, the back-reactions can then be neglected.

Overall rate constants ($k_{\text{tot}} = k_1 + k_2$) for the depletion of the starting material have been calculated

$$k_{\text{tot}} = k_1 + k_2 = \frac{2.303}{t} \log \left\{\frac{([\text{DEC}]/[\text{Std}])_f}{([\text{DEC}]/[\text{Std}])_0}\right\} \quad (1)$$

$$k'_{\text{tot}} = k'_1 + k'_2 = \frac{2.303}{t} \times \log\left\{\frac{[\text{DEC}]_f}{[\text{DEC}]_f + [C_2H_5OCH(CH_3)_2]_f + [C_2H_5OCHCH_2]_f}\right\} \quad (2)$$

from the gc analysis, based either on the internal standard (k) or on the amount of ether formed (k'); see eq 1 and 2, 0 and f denote initial and final concentrations, respectively. The observed first-order rate constants are shown in Table I together with the pertinent experimental data.

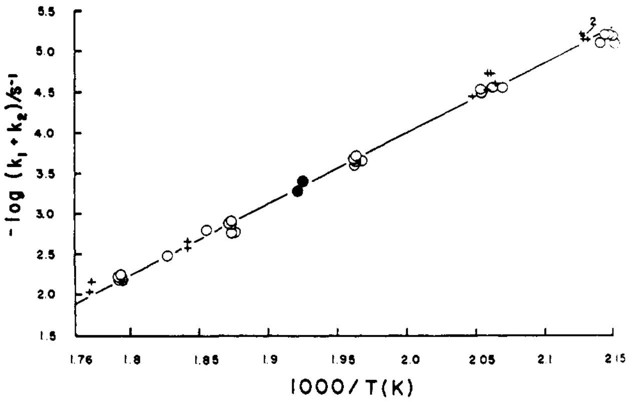


Figure 1. Arrhenius plot of the unimolecular rate constants $k_{\text{tot}} = k_1 + k_2$ for the pyrolysis of 2,2-dimethyl-3-ethoxycyclobutan-1-one in the gas phase. The reaction vessels used are indicated with open circles (glass), closed circles (packed glass vessel), and plus signs (Teflon-coated reactor). Numbers indicate overlapping points.

As can be seen from the entries in Table I, no systematic change in the overall rate constants with either the initial DEC pressure (5–50 Torr), the total starting pressure (including the internal standard), or the conversion (3.7 to 89%) attained is apparent. Addition of up to 670 Torr of propylene had no significant effect on the rate constants either. In Figure 1 an Arrhenius plot of the rate constants $k_{\text{tot}} = k_1 + k_2$ based on the internal standard method is shown and a similar plot with an only slightly larger apparent scatter of the data is obtained for $k'_{\text{tot}} = k'_1 + k'_2$.

The first set of experiments, carried out in a Teflon reactor, showed in the low-temperature range, in addition to the homogeneous elimination reaction represented by k'_1 and k'_2, a depletion of the starting material (DEC) *via* a unidentified heterogeneous route.

While the rate constants k'_{tot} (calculated from the amount of ether formed) were essentially consistent throughout the temperature range used in this study (compare Table I), the values obtained at temperatures of ~490 K and below for k_{tot} (based on the internal standard method) were up to four times too fast. In parallel with these fast rate constants (k_{tot}), pressure increases of only about 30% of the amount expected on the basis of the two ether products formed were observed. This partial heterogeneously induced depletion of the starting material only observed in the Teflon vessel and at low temperatures is attributed to the heterogeneously induced formation of higher molecular weight materials, probably due to a porous or incomplete coating of the vessel.

Replacing the Teflon vessel with glass vessels resulted in good consistency and agreement of the rate constants k_{tot} and k'_{tot} over the temperature range studied. The absence of considerable heterogeneous effects in Pyrex glass reactors was demonstrated by experiments carried out in a vessel packed with Pyrex glass tubing, resulting in a 35-fold increase of the surface to volume ratio. Within the experimental error

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(21) It is interesting to note, that these data imply a ring strain energy in cyclobutanone of only ~22.3 kcal mol^{-1} compared with ~26.2 kcal mol^{-1} for cyclobutane.

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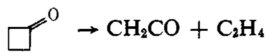
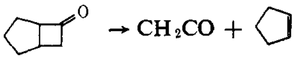
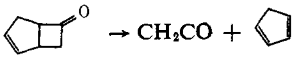
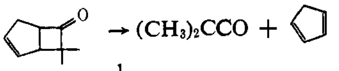
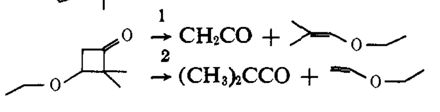
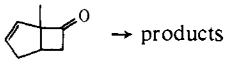
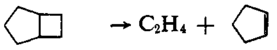
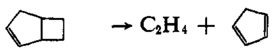
Table I. Kinetic Data for the Unimolecular Thermal Decomposition of 2,2-Dimethyl-3-ethoxycyclobutan-1-one (DEC) in the Gas Phase

		Start mat		Products		Conversion % of $[DEC]_0$[d]			
Temp,[a] °K	Time, min	P_{tot},[b] Torr	Mix[c]	$[DEC/Std]_f$[d]	[IEE/VEE][e]	Std[d,f,g]	Ether[h]	$k_{tot} \times 10^4$, sec^{-1}	$k'_{tot} \times 10^4$, sec^{-1}
464.3	995	68.3[k]	4	0.4425	3.32	51.15	33.96	0.1200[i]	0.0695
464.4	360	57.6	4	0.6686	3.35	24.97	11.7	0.1331[i]	0.0569
465.4	150	24.1	1	0.9320	3.00	19.04	4.79	0.2348[i]	0.0540
466.0	960	80.2[l]	3	0.5462	3.80	40.15	27.5	0.08914[i]	0.05574
466.8	129	66.1	3	0.7612	3.59	16.6	5.3	0.2344[i]	0.06992
467.7G	120	31.0[m]	3	0.8719	4.25	3.65	2.0	0.05759	
469.4G	940	22.4	4	0.597	2.74	33.53	30.01	0.0724	0.0633
469.6G	400	18.9	4	0.723	2.90	19.49	10.78	0.0903	0.0475
469.6G	436	18.2	4	0.703	2.20	21.56	13.71	0.0929	0.0564
469.6G	3847	31.1	4	0.2708	2.58	69.85	72.0	0.0520	0.0552
469.8G	990	23.1	4	0.6676	2.64	25.55	27.3	0.0497	0.0536
483.0	60	35.6	1	0.9112	3.16	22.36	8.9	0.7029[i]	0.2586
484.5G	120	22	4	0.7049	2.51	21.3	16.4	0.3333	0.2483
484.7	30	55.6	1	1.1092	2.70	4.65	4.57	0.2646	0.256
484.9G	215	26.1	4	0.7454	2.53	16.80	20.6	0.1426	0.1788
485.5G	300	28.8	4	0.674	2.48	25.1	28.1	0.1607	0.183
486.0G	940	19.8	4	0.2027	2.46	77.4	80.7	0.2636	0.292
486.6	70	46.3	1	0.8636	2.73	25.8	12.66	0.7090[i]	.3202
486.7	60	29.7	1	0.8801		25.0	9.7	0.7994[i]	0.2825
488.3G	60	20.5	4	0.7693	2.57	13.68	11.5	0.4087	0.3408
508.2	5	69.3	3	0.8403	2.66	7.11	6.3	2.460	2.180
509.2	10	60.8	3	0.8133	2.57	10.11	11.8	1.777	2.103
509.2	15	54.3	3	0.7684	2.48	15.08	15.8	1.816	1.912
509.2	30	50.6	3	0.5644	2.84	37.6	33.1	2.621	2.234
509.4	10	51.1	3	0.6609	2.82	30.5	14.25	5.232[i]	2.516
509.6	20.5	70.7	3	0.7667	2.73	23.3	22.5	2.160	2.072
510.1	5		1	1.080		7.17		2.480	
511.5	70		1	0.5313	*j*	54.53		1.876	
513.8	45	44.1	1	0.6804	*j*	41.76		2.003	
514.7	90	42.8	1	0.3402	*j*	70.88		2.285	
514.9	30		1	0.6184	*j*	44.79		3.301	
515.1	10		1	0.916	*j*	21.6		4.048	
519.1P	30	34	4	0.4192	2.34	53.3	51.0	4.225	3.965
520.1P	60	13	4	0.0977	2.70	89.1	84.1	6.160	5.101
531.1	5	18.4	1	0.8225	*j*	28.6		11.23	
532.9	7	28.7	2	0.4020	2.83	60.04	50.67	21.84	16.82
533.0	4	39.4	2	0.6564	2.46	34.75	15.3	17.79	6.89[i]
533.5	5	56.3	2	0.6655	2.75	33.84	30.1	13.77	11.92
533.6	2		2	0.7778		22.85	15.1	21.62	13.59
533.7	3		2	0.6811		32.43	26.7	21.78	17.26
534.1	10	41.6	2	0.4046	(3.29)	59.78	41.15	15.18	13.00
538.8	5	35.4[n]	3	0.6078	(3.81)	39.22	35.71	16.60	15.71
542.8G	5	24.4	4	0.5091	3.60)	43.2	56.4	18.84	27.67
543.0G	10	28.9	4	0.3877	2.06	58.95	65.3	21.28	25.29
545.9	3	28.9	1	0.7815	*j*	32.16		21.56	
546.1	4	26.9	1	0.6210	*j*	46.14		25.78	
546.8	2	21.0	1	0.8584	*j*	14.16		24.52	
547.2	4	42.3	1	0.5984	2.11	48.18	54.3	27.40	32.62
547.4	6	46.0	1	0.5269	*j*	54.37		21.80	
547.6	5	48.8	1	0.4019	*j*	65.2		35.19	
548.7	7	26.7[o]	1	0.6210	*j*	75.86		33.85	
548.8	5	36.4	1	0.5409	*j*	53.2		25.29	
557.2	3	62.2	3	0.1599		82.33	83.33	96.31[i]	99.58[i]
557.4	2	58.1	3	0.5142	2.15	48.58	51.74	55.45	60.72
557.5	1.5		3	0.5283	(2.94)	41.58	42.4	59.75	61.3
557.6	1	71.9	3	0.7467	2.56	25.33	28.55	48.70	56.03
558.1	3	75.0	3	0.3204	2.18	64.60	67.50	57.70	62.46
558.2	2.5	68.7	3	0.3893	2.31	56.98	59.62	56.25	60.46
558.2	1.5	41.8	3	0.5381	2.04	40.53	42.77	57.75	62.02
564.8G	1.5	20.0	4	0.4517	2.00	51.5	53.44	77.36	84.94
564.9G	4	24.4	4	0.1654	2.53	81.75	86.94	70.89	84.82

[a] Experiments were carried out in a Teflon-coated stainless-steel reactor of 805 cm^3 volume except where marked with a G (2060-cm^3 cylindrical Pyrex glass reactor) or a P (1340 cm^3 cylindrical Pyrex glass reactor, filled with Pyrex glass tubing). [b] Total pressure, including the added internal standard. [c] Four different mixtures of the starting material DEC[d] with the internal standard (Std)[d] have been used, with the initial ratios $[DEC]_0/[Std]_0$ = (1) 1.16 ± 0.01, (2) 1.00 ± 0.01, (3) 0.911 ± 0.007, (4) 0.902 ± 0.010. [d] DEC stands for 2,2-dimethyl-3-ethoxycyclobutan-1-one and Std for the internal standard, *p*-ethyltoluene. Initial and final concentrations are denoted with 0 and f, respectively. [e] Ratio of isobutenyl ethyl ether to vinyl ethyl ether based on the gas-chromatographic analysis. [f] Total of the ketenes identified as their methanol addition products methyl acetate and methyl methylpropionate. [g] Based on the depletion of the starting material as obtained from the gas-chromatographic analysis using the internal standard method. [h] Based on the formation of isobutenyl ethyl ether and vinyl ethyl ether obtained from the gas-chromatographic analysis. [i] Not used for least-squares analysis due to surface effects. Compare text. [j] The work-up procedure used in these experiments precluded the measurement of the relative concentrations of the two ethers. Compare text. [k–o] Propylene added amounting to 351,[k] 88,[l] 143,[m] 394,[n] and 669[o] Torr.

Table II. Activation Parameters for the Unimolecular Thermal Decomposition of Cyclobutanone Derivatives and Related Hydrocarbons in the Gas Phase

	Reaction	Log (A/sec^{-1})	E_a, kcal mol^{-1}	Ref
A	 → $CH_2CO + C_2H_4$	14.6 14.55	52.0 51.9	a b
B	 → CH_2CO +	14.21 ± 0.10	48.55 ± 0.29	19
C	 → CH_2CO +	13.16 ± 0.11	37.52 ± 0.25	17
D	 → $(CH_3)_2CCO$ +	12.90 ± 0.22	37.71 ± 0.52	18
E	 1 → CH_2CO + 2 → $(CH_3)_2CCO$ +	13.61 ± 0.22	40.32 ± 0.51	This work
F	 → products	14.50 ± 0.28	43.94 ± 0.66	6
G	 → $2C_2H_4$	15.6	62.5	31
H	 → C_2H_4 +	14.8	60.7	32
I	 → C_2H_4 +	14.3	49.0	33

[a] M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Amer. Chem. Soc.*, **76,** 6271 (1954). [b] T. H. McGee and A. Schleifer, *J. Phys. Chem.*, **76,** 963 (1972).

limits the observed rate constants throughout the temperature range were the same as those obtained from experiments carried out in unpacked reaction vessels.

In the temperature range 400–565 K about 50 ± 20% of the pressure changes expected on the basis of the ether conversion (Table I, column 8) were observed for both glass and Teflon vessels, reflecting the thermal instability of the ketene products under the reaction conditions used, as was previously observed for similar systems.[6a,17,19]

The partial loss of ketene and 1,1-dimethylketene is also apparent from the observed gc product ratios of vinyl ethyl ether (VEE) to methyl methylpropionate (MMP) and isobutenyl ethyl ether (IEE) to methyl acetate (MA), which should equal 1.00 following the stoichiometry of reaction systems I and II.

[VEE]/[MMP] ratios ranging between 1.24 and 2.33 and [IEE]/[MA] values between 0.91 and 2.25 were observed yielding average values (36 experiments) of 1.56 and 1.25, respectively. These data imply that on average 36% of the ketene and 20% of the 1,1-dimethylketene formed are lost during the reaction, presumably *via* oligomerization routes. This is perfectly in line with observations from the liquid-phase ketene addition reactions to olefins, whereby ketene itself undergoes faster dimerization and oligomerization reactions compared with 1,1-dimethylketene.

Using a least-squares analysis, two independent sets of activation parameters have been calculated from the observed rate constants. The values of k_{tot} (based on the internal standard method) listed in Table I (disregarding all the data obtained in the Teflon vessel below 409 K) yield

$$\log (k_{tot}/\text{sec}^{-1}) = \log (k_1 + k_2/\text{sec}^{-1}) = (13.58 \pm 0.29) - (40.27 \pm 0.68 \text{ kcal mol}^{-1})/\theta$$

The corresponding data obtained for the rate constants based on the amount of the two ethers formed (k'_{tot}) give

$$\log (k'_{tot}/\text{sec}^{-1}) = \log (k'_1 + k'_2/\text{sec}^{-1}) = (13.61 \pm 0.22) - (40.32 \pm 0.51 \text{ kcal mol}^{-1})/\theta$$

where $\theta = 2.303RT$ and errors are standard deviations.

The overall reliability of the kinetic data and analysis of the system is documented with the good agreement of these two independent sets of Arrhenius parameters based on the depletion of the starting material as well as the formation of the (thermally stable) ether product with time. The secondary oligo- and polymerization reactions of the ketene products observed throughout this study evidently do not involve the starting material to any kinetically significant amount in contrast to the heterogeneous component observed at low temperatures in the Teflon vessel.

Considering that both ethers VEE and IEE, are thermally stable at the reaction conditions used, the ratio of IEE/VEE should directly equal k_1/k_2. In column 6 of Table I the observed ratios of IEE/VEE are listed. Despite the large scatter of the data, ranging overall between 3.8 and 2.0, a trend toward lower values with increasing temperature is apparent, and it is best represented by $\log (k_1/k_2) = (0.1 \pm 0.5) - (1.0 \pm 0.8 \text{ kcal mol}^{-1})/\theta$.

Discussion

The activation parameters for the thermal unimolecular decompositions of cyclobutanone derivatives are listed together with the data for the corresponding hydrocarbons in Table II.

As mentioned in the introductory section,[17-19] the thermal decomposition of cyclobutanone derivatives in the gas phase follows a molecular elimination path (reactions A–E, Table II) outlined in eq I–III involving a concerted mechanism and an orthogonal *polar* transition-state structure.

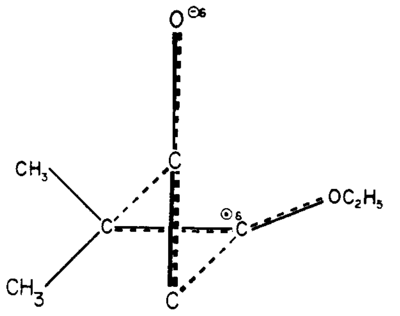
Thermally induced heterolytic or quasi-heterolytic processes in the gas phase are generally disfavored compared to homopolar reaction routes as heteropolar bond dissociation energies BDE ($A^+ \cdots B^-$) considerably exceed the homopolar BDE ($A \cdots B$) values. Thermal reactions in the gas phase, which are essentially controlled by a change in relative charge densities in the molecule in going from the ground to the transition state, are only expected for multicenter but not for two-center transition-state complexes. One "model" class of reactions proceeding *via* a multicenter polar reaction path is the elimination of HX from alkyl halides and related reactions, shown to involve a *quadrupolar* semi-ion pair type transition-state structure.[24,25] The ($_{\pi}2_a + {}_{\pi}2_s$) ketene + olefin reaction appears to be part of another class of thermally induced polar multicenter gas-phase reactions[26] involving an effectively *zwitterionic* rather than quadrupolar charge separation in the gaseous transition state.

Accepting the concept of a concerted polar reaction mechanism, the observed activation parameters for system A–D shown in Table II can be interpreted to demonstrate the absence of significant differences in charge densities on the center D (eq I) between the ground and transition states, and a stabilizing effect onto center C in the transition state of 11 kcal mol^{-1} for a vinyl group and about 3 kcal mol^{-1} for an alkyl group. This work yields for the ethoxy substituent on center C a stabilizing effect of about 12 kcal mol^{-1}.

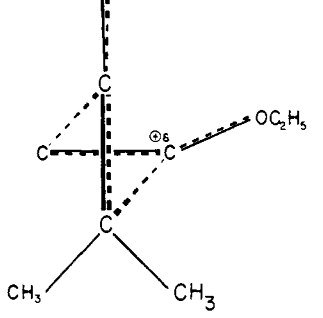
All these data are consistent with the formation of a quasi-zwitterionic charge separation, rather than a more even quadrupolar-type charge distribution over the reactive centers. To a first approximation the observed stabilizing effects may be compared with those for the corresponding gaseous molecular ions.[28] Based on the following differences in heats of formation $\Delta(\Delta H_f°)$ (in kcal mol^{-1}) between molecular ions and molecules,[29] $C_3H_6^+ - C_3H_6 = 224$, $(CH_3)_2O^+ - (CH_3)_2O = 230$, and $C_3H_8^+ - C_3H_8 = 255$ apparent stabilization energies of 26 and 32 kcal mol^{-1} for a vinyl or methoxy substituent, respectively, can be calculated.

On the basis of this analysis it then appears reasonable that alkoxy and vinyl substituents exercise about the same effect *via* a partial cation stabilization amounting to approximately one-third the full cation stabilization energy.

The proposed transition-state structures involved in reactions II and III are pictured as X and Y, respectively. On the basis of both the anticipated steric interactions in the transition state and the dissociation energies of the bonds involved, one would expect very similar competitive rates as is indeed found. It appears that the formation of TS I is slightly favored (~1 kcal mol^{-1}) energetically over TS II.



X



Y

The preexponential factor of $10^{13.6}$ sec^{-1} observed in this work is perfectly in line with those of the systems A–D listed in Table II. The apparent entropy loss of ~4.5 kcal^{-1} mol^{-1} when compared with cyclobutanone is consistent[17] with a partial stiffening of the ethoxy rotor due to partial cation "resonance." Compared with the bicyclic systems C and D (for which an additional entropy loss in the orthogonal transition state structure from the intramolecular interaction of the two π systems was postulated[17,18]) a higher A factor was to be expected.

It is interesting to note that substitution of a hydrogen atom by a vinyl group on carbon center A (eq I) rather than C was found to have a remarkably different effect, as would be expected in view of the postulated zwitterion type transition state. The study of the pyrolysis of 7,7-dimethylbicyclo[3.2.0]hept-2-en-6-one[6] (reaction system F in Table II) revealed a variety of products, most of which probably arrive from the linear ketene obtained as a primary product *via* route b in eq I.[6] Comparing the activation energies observed for systems B and F, the stabilizing effect of a vinyl group onto the center A (carrying a negative charge, if any) appears to be about 5 kcal mol^{-1}. The origin of this stabilization energy and the detailed reaction mechanism operative in the pyrolysis of cyclobutanone derivatives carrying functional groups on the carbon center A (eq I) are not yet satisfactorily understood.

In contrast with the cyclobutanone derivatives the observed activation parameters for the analogous cyclobutane hydrocarbons (G–I in Table II) can be consistently explained with a biradical mechanism.[30–32]

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(25) S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, 87, 4036 (1965).

(26) Based on liquid-phase studies Huisgen, *et al.*,[27] proposed that polycyanoolefin cycloadditions also fall in this category.

(27) R. Huisgen and G. Steiner, private communications, 1972.

(28) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," U. S. National Bureau of Standards, NSRDS-NBS 26, 1969.

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(32) A. T. Cocks and H. M. Frey, *J. Chem. Soc. A*, 2564 (1971).