irradiation of propionaldehyde in perfluoromethylcyclohexane: α cleavage; and hydrogen abstraction from a ground state aldehyde molecule. The relative importance of these processes cannot be determined conclusively from our results.

Acknowledgment. This work has been supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society. The authors are grateful to the referee for bringing their attention to ref 17.

Photoionization Mass Spectrometer Studies of Gas Phase Ozone–Olefin Reactions

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Abstract: The room temperature gas phase reactions of ethylene, *cis*-2-butene, and isobutene with ozone at pressures of *ca.* 2 Torr have been investigated using photoionization mass spectrometry. Both radical species and stable products were identified and were followed as a function of time. The implications of these observations to the mechanism of gas phase ozone–olefin reactions are discussed.

This investigation of the intermediates and products of the reaction of selected olefins (ethylene, *cis*-2-butene, and isobutene) with ozone using photoionization mass spectrometry was undertaken as part of a larger study dealing with the chemiluminescence observed in these reactions and its relationship to the overall reaction mechanism. Previous room temperature studies of the chemiluminescence at approximately 2 Torr total pressure, to be reported in more detail later, have identified the emitting species common to all three reactions as electronically excited formaldehyde($^1A''$) and OH($A^2\Sigma^+$) as well as the Meinel band emission from vibrationally excited OH radicals.[1–5] The similarity of the OH Meinel band emission to that from the well-known reaction[6–8]

$$H + O_3 \longrightarrow OH_{\nu}{}^{\dagger}{}_{\leq 9} + O_2$$

suggests the presence of H atoms in these reactions. In the *cis*-2-butene reaction a fourth emission at 520 nm has been tentatively identified as glyoxal phosphorescence ($^3A_u \rightarrow {}^1A_g$).

While much excellent work on the overall kinetics, final products, and mechanisms of gas phase ozone–olefin reactions has been done over a wide range of reactant concentrations,[9–18] the intermediates, and hence the detailed mechanisms, remain obscure. For example, the Criegee mechanism of ozonolysis, which has been established to be a major reaction pathway in the liquid phase,[19] has generally been applied to the gas phase reactions. Thus, the formation of a number of the observed stable products can be rationalized in terms of the decomposition and reactions of the Criegee "zwitterion" (or biradical in the gas phase). However, direct evidence for its existence in the gas phase is lacking, as indeed it is in the liquid phase. In addition, the anomalous effects of reactant concentration on the experimentally determined rate constants[11–13,15–17] remain unexplained.

Ozone–olefin reactions are known to be involved in the formation of photochemical smog. However, because of the paucity of data on the intermediates and mechanisms of these reactions, little is known about the detailed interaction of these intermediates and products with other atmospheric constituents.[20] While these reactions have been postulated to act as a source of chain carrying OH radicals,[20] it is only recently that any evidence for their production from low pressure ozone–olefin reactions has been obtained.[1] Thus, the elucidation of these reaction mechanisms is of importance to both fundamental and applied chemistry.

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(1) B. J. Finlayson, J. N. Pitts, Jr., and H. Akimoto, *Chem. Phys. Lett.*, **12**, 495 (1972).

(2) W. A. Kummer, J. N. Pitts, Jr., and R. P. Steer, *Environ. Sci. Technol.*, **10** (5), 1045 (1971).

(3) J. N. Pitts, Jr., W. A. Kummer, R. P. Steer, and B. J. Finlayson, *Advan. Chem. Ser.*, **No. 113**, 246 (1972).

(4) J. N. Pitts, Jr., B. J. Finlayson, H. Akimoto, W. A. Kummer, and R. P. Steer, International Symposium on the Identification and Measurement of Environmental Pollutants, June 14–17, Ottawa, Canada, 1971.

(5) J. N. Pitts, Jr., B. J. Finlayson, and R. Atkinson, submitted for publication.

(6) J. D. McKinley, Jr., D. Garvin, and M. J. Boudart, *J. Chem.* Phys., **23**, 784 (1955).

(7) L. F. Phillips and H. I. Schiff, *J. Chem. Phys.*, 37, 1233 (1962).

(8) P. E. Charters, R. G. MacDonald, and J. C. Polanyi, *Appl. Opt.*, **10**, 1747 (1971).

(9) W. E. Scott, E. R. Stephens, P. L. Hanst, and R. C. Doerr, *Proc. Amer. Petrol. Inst.*, 3 (37), 171 (1957).

(10) B. E. Saltzman, *Ind. Eng. Chem.*, **50**, 677 (1958).

(11) T. Vrbaski and R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1053, 1063 (1960).

(12) Y. K. Wei and R. J. Cvetanovic, *Can. J. Chem.*, **41**, 913 (1963).

(13) J. J. Bufalini and A. P. Altshuller, *Can. J. Chem.*, **43**, 2243 (1965).

(14) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, 1961, and references therein.

(15) D. H. Stedman, C. H. Wu, and H. Niki, Scientific Research Staff, Ford Motor Co., 1972.

(16) W. B. DeMore, *Int. J. Chem. Kinet.*, **1**, 209 (1969).

(17) R. A. Cox and S. A. Penkett, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1735 (1972).

(18) P. L. Hanst, E. R. Stephens, W. E. Scott, and R. C. Doerr, Symposium on Air Pollution Research, Division of Petroleum Chemistry, Vol. 4, Sept. 1959.

(19) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958), and references therein.

(20) H. Niki, E. E. Daby, and B. Weinstock, *Advan. Chem. Ser.*, **No. 113**, 16 (1972).

Clearly, identification of the intermediates and labile as well as stable products is necessary in order to permit the formulation of a detailed reaction mechanism. Photoionization mass spectrometry offers several advantages in this regard.[21–23] First, the use of a low energy ionization source makes it feasible to detect radical species produced in the reaction, free of the fragmentation problems encountered with electron beam ionization. In addition, variation of the photoionizing resonance lamps allows selective photoionization of the species.

In this work it was therefore our purpose to detect and study the kinetics of the intermediates and products of the reaction of ozone which ethylene, *cis*-2-butene, and isobutene in order to clarify the chemiluminescent reaction steps and their relationship to the overall reaction mechanism.

Experimental Section

The experimental system has been described in detail previously.[21] The fast flow system (i.d. = 11 mm) had a moveable inlet jet (o.d. = 4 mm) through which the olefin was added axially. By throttling the pumping system, the reaction time could be varied over the range ~1–130 msec. The pressure at the midpoint of the moveable inlet region was monitored by an MKS Barytron pressure gauge.

The gas in the flow system was sampled *via* a pinhole into the photoionization chamber of a quadrupole mass spectrometer. The ions were detected by a Cu–Be electron multiplier and ion counts were displayed digitally with provision for varying counting intervals. Xe, Kr, or Ar microwave powered resonance lamps[24] were used as photoionization sources. The ionizing energies of these lamps are shown in Figure 1 together with the ionization potentials[25] of some stable molecules and free radicals of interest in this study; selective photoionization can therefore be achieved by the appropriate use of these lamps.

All experiments were carried out at total pressures of approximately 2 Torr. Typical partial pressures of reactants were 0.04 Torr of O_3 and 0.3 Torr of the olefin. Approximately 2% O_3 in O_2 flows were obtained by the passage of Matheson ultrahigh purity grade O_2 (>99.99%) through a Welsbach Model T-408 ozonator. The olefins were all of research grade purity (>99.8%) and were used without further purification. Fully deuterated 2-butene (mixture of cis and trans) was obtained from Merck Sharp and Dohme with stated D atom purity levels >99%. A bypass system enabled the O_3–O_2 gas flow to be replaced by a pure O_2 stream.

Results

In all experiments, background counts were taken (typically an average of several 10-sec counts) with O_2–olefin mixtures, and these were subtracted from the ion counts obtained in the presence of O_3. All counts were corrected for decay of the lamp intensity and small fluctuations in olefin concentration by monitoring a suitable impurity peak or the parent peak (generally C_2H_4 which occurred as an impurity in the *cis*-2-butene and isobutene).

The *m/e* scale was corrected for any nonlinearity using parent peaks of authentic compounds. The Kr lamp was used in the majority of experiments, while the Xe resonance lamp was used to selectively photoionize and hence identify the radicals C_2H_5 (*m/e* 29), CH_3CO, and/or C_3H_7 (*m/e* 43). The Ar lamp was used for the species HO_2, H_2O_2, HCHO, CH_3OH, and HCOOH which are not photoionized by either the Xe or Kr lamps (Figure 1).

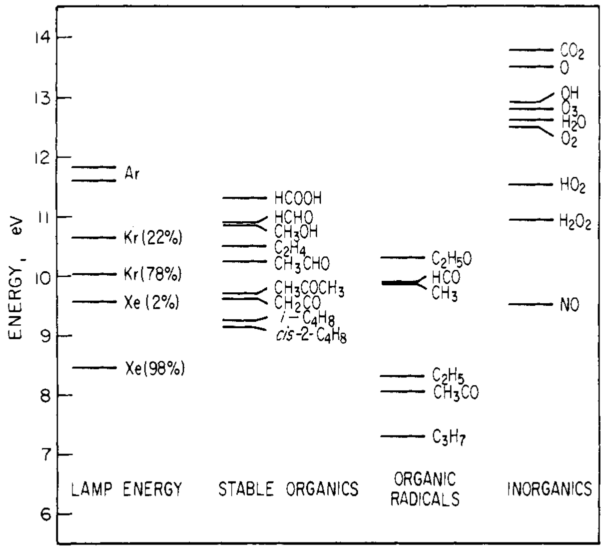

Figure 1. Resonance lamp energies and ionization potentials of relevant species.

A. ***cis*-2-Butene.** Table I shows the observed product mass numbers together with the lamps with which they were observed at reaction times of ~130 msec. Column 3 of Table I gives the possible species for each mass observed. Positive identification was obtained in some cases by a combination of deuteration, kinetic behavior, and the use of various photoionization lamps. For example, with the Kr lamp, a peak was observed at *m/e* 29. In the present system this could be due to HCO or C_2H_5. On deuteration, the *m/e* 29 peak shifted to *m/e* values of 30 and 34, indicating both HCO and C_2H_5. Replacement of the Kr lamp by an Xe lamp showed a mass peak at *m/e* 29 confirming the presence of C_2H_5 (see Figure 1); furthermore, the kinetic time dependence was that expected for a radical intermediate as shown in Figure 3b. Column 4 of Table I thus shows the species identified by procedures similar to that described above.

For the peaks of *m/e* 29–47 inclusive, and for 104, their time dependent behavior and their dependence on olefin concentration were determined. Figures 2 and 3 show the observed time dependence of these product peaks. For the peak at *m/e* 104, deuteration showed the presence of eight H atoms, hence the formula $C_4H_8O_3$ (Table I). The observed linear dependence on both time and olefin concentration shown in Figure 4 indicated that this was a stable molecule over this time range. In general, the kinetic behavior confirms the identifications of Table I; *i.e.*, stable products increase linearly with time, while radical intermediates show an approach to a steady state. However, in certain cases, *i.e.*, *m/e* ratios of 43, 45, and 47, anomalous behavior is observed as shown in Figure 2b. Experiments using a Xe lamp with a sapphire window (transmitting only the 8.44-eV line) gave no evidence for an *m/e* 43 peak. This observation, in conjunction with the observed kinetics, strongly suggests that this peak, and by analogy possibly those at *m/e* 45 and 47, arises from fragmentation in the mass spectrometer of more complex molecules whose ionization potentials are in the range $9.57 \geq IP \geq 8.44$ eV.

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[21] I. T. N. Jones and K. D. Bayes, *Symp. (Int.) Combust., [Proc], 14th* (1972).

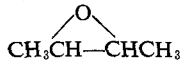
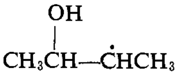
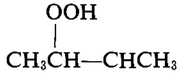
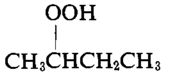
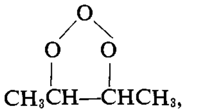
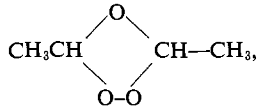
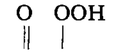
[22] I. T. N. Jones and K. D. Bayes, *J. Amer. Chem. Soc.*, **94**, 6869 (1972).

[23] J. R. Kanofsky and D. Gutman, *Chem. Phys. Lett.*, **15**, 236 (1972).

[24] H. Okabe, *J. Opt. Soc. Amer.*, **54**, 478 (1964).

[25] R. W. Kiser, "Introduction to Mass Spectrometry and Its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965.

Table I. Observed Peak Mass Numbers and Their Assignments

Obsd mass no. *m/e*	Lamp	Possible species[a]	Definite identification	Means of identification[b]
		cis-2-Butene		
29	Kr, Xe	HCO, C_2H_5	HCO and C_2H_5	D, L, K
30	Ar	HCHO	HCHO	L
32	Ar	CH_3OH, $O_2(^1\Delta)$	CH_3OH[c]	K
33	Ar	HO_2	HO_2	L, K
34	Ar	H_2O_2	H_2O_2	L
42	Kr	CH_2CO, C_3H_6	CH_2CO	D, K
43	Ar, Xe	CH_3CO, C_3H_7	*d*	
44	Kr	CH_3CHO	CH_3CHO	D, K
45	Kr	C_2H_5O, HCO_2	C_2H_5O	D
46	Ar	HCOOH	HCOOH	L
47	Kr	CH_3O_2	CH_3O_2	D
58	Kr	$(CHO)_2$, CH_3COCH_3 C_2H_5CHO	$(CHO)_2$	D
70	Kr	$CH_3COCH{=}CH_2$	*a*	
72	Kr	$CH_3COC_2H_5$ or 	*a*	
73	Kr	C_4H_9O,  $CH_3\overset{OH}{C}H{-}\dot{C}HCH_3$	*a*	
75	Kr	$C_3H_7O_2$, $CH_3C(O)OO$	*a*	
88	Kr	$CH_3COCHOHCH_3$, $CH_3CH(OCH_3)CH_2CH_3$	*a*	
89	Kr	$C_4H_9O_2$,  $CH_3\overset{OOH}{C}H{-}CHCH_3$	*a*	
90	Kr	 $CH_3\overset{OOH}{C}HCH_2CH_3$	*a*	
91	Kr			
104	Kr	   $CH_3\overset{O}{\overset{\|}{C}}{-}\overset{OOH}{C}HCH_3$	*a*	
107	Kr	$C_3H_7O_4$, $C_2H_3O_5$		
		Ethylene		
30	Ar	HCHO	HCHO	L, K
43	Kr, Xe	CH_3CO, C_3H_7	CH_3CO[e]	L, K
		Isobutene		
30	Ar	HCHO	HCHO	L, K
42	Kr	CH_2CO, C_3H_6		
43	Kr, Xe	CH_3CO, C_3H_7	*d*	
44	Kr	CH_3CHO	CH_3CHO	
58	Kr	CH_3COCH_3, $(CHO)_2$ C_2H_5CHO	*f*	
59	Kr			

[a] For high mass numbers ($m/e \geq 70$) there are several possible structures which cannot be differentiated; typical structures are given which include those products expected from the reaction scheme given in the text (see Discussion). [b] D = deuteration, L = selective use of lamps, K = kinetic behavior (see text). [c] On the basis of published rate constants for $O_2(^1\Delta) + O_3 \rightarrow O + 2O_2$ [F. D. Findlay and D. R. Snelling, *J. Chem. Phys.*, **54**, 2750 (1971)] the kinetic behavior observed is that expected of CH_3OH rather than of $O_2(^1\Delta)$. [d] On use of Xe lamp with sapphire window (see text), this mass number was not observed. [e] C_3H_7 would have to be formed by radical attack on C_2H_4, and these reactions are expected to be slow compared with radical reactions with O_3 and O_2. [f] On the basis of the known chemistry of isobutene–O_3 reactions,[11–13] acetone is by far the most likely product.

It is seen from Figure 3a that the HCOOH and H_2O_2 signals tend to level off at the longer time regions. This may be due to diffusion to and subsequent absorption on the wall. Average diffusion times to the walls were calculated to be ~6 msec.

The signals obtained here, although corrected for decay of lamp intensity and fluctuations in the olefin pressure within a given series of runs, are uncorrected for relative photoionization efficiencies of the species and differences in photon intensities of the resonance lines used. Thus, for example, although the signals from CH_2CO and CH_3CHO are similar (Figure 3a), CH_3CHO is photoionized only by the higher energy Kr line (Figure 1), which is typically present[24] to the extent of 22% of the combined 10.64- and 10.03-eV Kr lines. Therefore, assuming equal photoionization efficiencies,

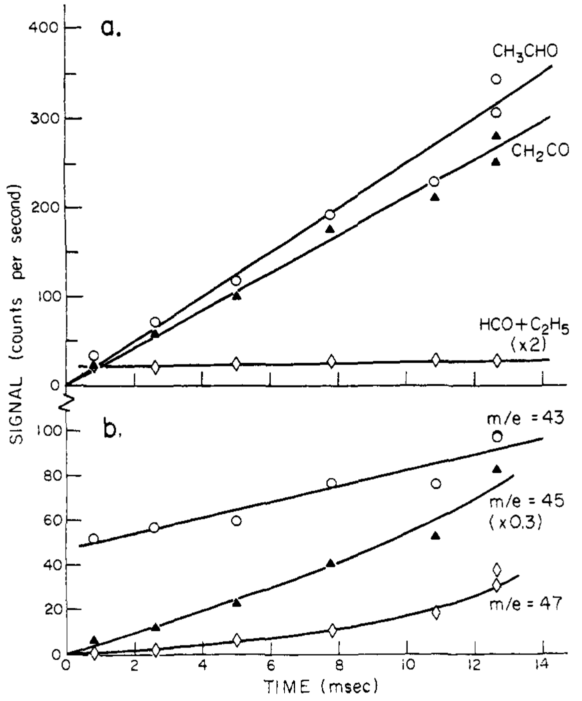


Figure 2. Kinetic behavior of some species observed in the *cis*-2-butene–ozone reaction using a krypton lamp: (a) HCO + C_2H_5 (*m/e* 29), CH_2CO (*m/e* 42), and CH_3CHO (*m/e* 44); (b) mass peaks *m/e* 43, 45, and 47.

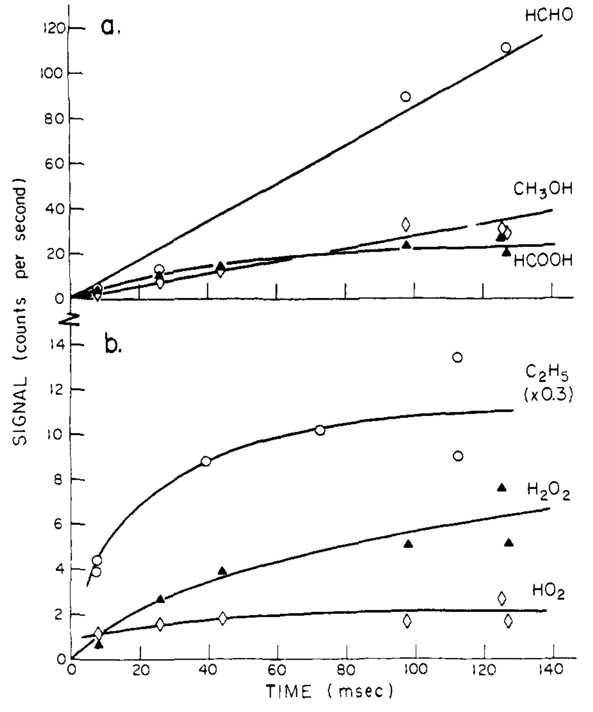


Figure 3. Kinetic behavior of some species observed in the *cis*-2-butene–ozone reaction: (a) HCHO (*m/e* 30), CH_3OH (*m/e* 32), and HCOOH (*m/e* 46) using an argon lamp; (b) C_2H_5 (*m/e* 29) using a xenon lamp, HO_2 (*m/e* 33) and H_2O_2 (*m/e* 34) using an argon lamp.

the yield of CH_3CHO becomes approximately five times that of CH_2CO. Using a rate constant of 9×10^4 l. mol^{-1} sec^{-1} for the reaction of ozone with *cis*-2-butene as measured under similar experimental conditions,[5] the amount of ozone reacted over the time interval of 130 msec will be ~15% or 3×10^{-7} mol l.$^{-1}$.

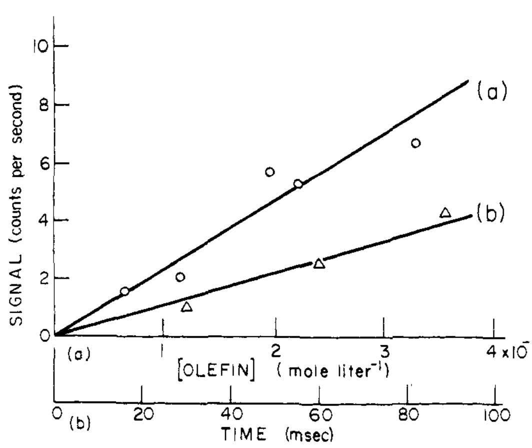


Figure 4. Dependence of signal at *m/e* 104 on (a) olefin concentration and (b) time, using a krypton lamp in the *cis*-2-butene–ozone reaction.

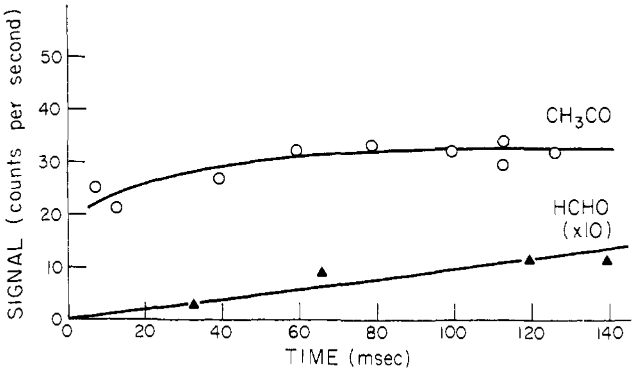


Figure 5. Kinetic behavior of HCHO (*m/e* 30) (argon lamp) and CH_3CO (*m/e* 43) (xenon lamp) in the ethylene–ozone reaction.

With unit stoichiometry[15,17] this corresponds to 3×10^{-7} mol l.$^{-1}$ *cis*-2-butene reacted or ~2% of the initial *cis*-2-butene concentration. From the photoionization mass spectrometer sensitivity, it can be calculated that the observed CH_3CHO ion counts correspond (within a factor of 2) to ~3×10^{-7} mol l.$^{-1}$ of CH_3CHO after a 130-msec reaction. Hence, within these error limits, ~1 mol of CH_3CHO is produced per mole of *cis*-2-butene reacting, which is in agreement with previous workers.[11,12]

B. Ethylene. The product mass peaks observed at reaction times of ~130 msec are shown in Table I. Again, use of the various resonance lamps provided confirmatory identifications. Figure 5 shows the time-dependent behavior of the *m/e* 43 peak (presumed to be CH_3CO) using a Xe lamp and of HCHO. The CH_3CO shows the kinetic behavior expected for a radical intermediate, attaining a steady state. Furthermore, the *m/e* 43 peak remained, within experimental error (13 ± 11 counts above a background of ~10 counts per 10 sec), on use of a Xe lamp with a sapphire window. Deuteration was not feasible because of the generally very weak signals.

C. Isobutene. Table I shows the mass peaks observed at reaction times of ~130 msec, together with the lamps with which they were observed. The kinetic time dependence of the mass peaks is shown in Figure 6. As in the case of O_3 + *cis*-2-butene the *m/e* 43 peak showed anomalous behavior, increasing with time

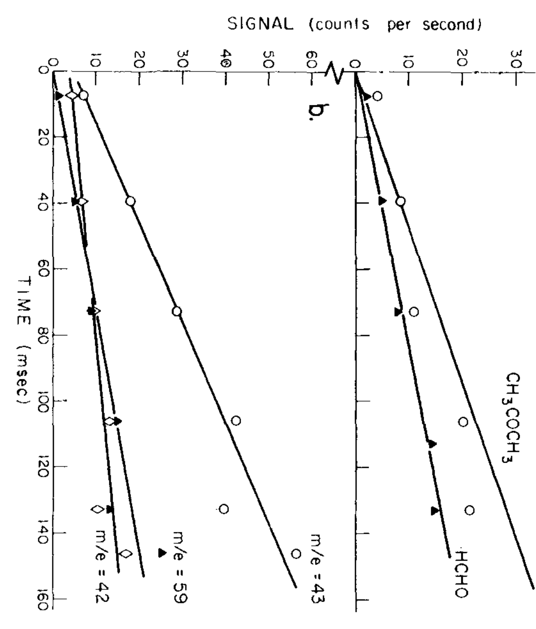


Figure 6. Kinetic behavior of some species in the isobutene–ozone reaction: (a) HCHO (*m/e* 30) (argon lamp) and CH_3COCH_3 (*m/e* 58) (krypton lamp); (b) mass peaks *m/e* 42, 43, and 59 using a krypton lamp.

(Figure 6b). Use of a Xe lamp with a sapphire window showed no evidence for *m/e* 43, again suggesting that it arises from fragmentation of a more complex molecule in the mass spectrometer. Similarly, as seen in Figure 6b, the time dependence of *m/e* 42 (CH_2CO or C_3H_6) suggests that it also arises by fragmentation; stable products are expected to increase linearly from a zero ordinate.

No identification could be made for *m/e* 59, and deuteration was not attempted because of the low counts obtained and because of interference that would have occurred from *i*-C_4D_8 at *m/e* 64.

Subsidiary experiments were carried out with acetone and acetaldehyde to determine if CH_3CO arose from fragmentation of these molecules in the mass spectrometer. A small amount of fragmentation was observed. The ratio of the signals at *m/e* 58:43 was approximately 30:1. Thus this cannot account for the *m/e* 43 signals observed in this work.

Discussion

The majority of the data was obtained for the *cis*-2-butene–ozone reaction because of its higher constant[5,11-13,17] and therefore larger observable percentage reaction as compared to the ethylene and isobutene reactions.

The stable products observed at these short reaction times are compared in Table II with selected previous product studies reported in the literature. It is seen that there is good agreement with the major products observed: formaldehyde from ethylene, acetone from isobutene, and acetaldehyde from *cis*-2-butene. Also included in Table II are qualitative estimates from this work of the product yields using the observed ion counts as a measure of concentration. In certain cases minor amounts of products not listed in Table I may have been present. For example, in the *cis*-2-butene–ozone reaction, propylene could have been present in

Table II. Stable Products Observed in the Reaction of Ozone with Ethylene, Isobutene, and *cis*-2-Butene[a]

Olefin	HCHO	CH_3CHO	CH_3COCH_3	CH_2CO	*i*-C_3H_7CHO	MF[b]	$(CHO)_2$	C_3H_6	C_3H_8	HCOOH	CH_3OH	H_2O_2	CO_2	CO	H_2O	Ref
C_2H_4		0.019								0.25						11
	0.53									<0.03			0.13	0.88	0.88	9
	Major															This work
i-C_4H_8			0.53		0.005	0.005		0.005	0.009	0.66	0.013		0.37			11
		0.008	0.52										0.35			12
	Major		Major													This work
cis-C_4H_8-2		1.02						0.023		0.20	0.152		0.42			11
		0.98											0.35			12
	Major	Major		Major			Minor			Minor	Minor	Minor				This work

[a] Product yields are given as the number of moles of product per mole of ozone consumed. [b] MF = methyl formate.

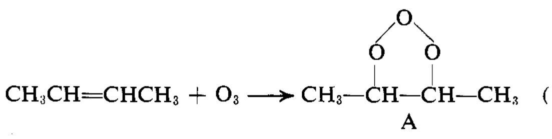
small amounts along with much larger quantities of ketene. In this work, several of the anticipated products such as CO, CO_2, H_2, and H_2O cannot be detected with photoionization mass spectrometry (Figure 1). In addition, it was not possible to detect the OH radical which is known[1] to be present in the low pressure O_3–olefin reactions.

On the basis of the observed products and their kinetics in the *cis*-2-butene oxidation, some of the reaction steps can be tentatively identified as shown below. Reactions which are slow under these experimental conditions compared to other available reaction paths have been omitted; for example, the three-body reaction[26, 27]

$$H + O_2 + M \longrightarrow HO_2 + M$$

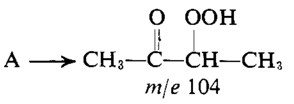
has been omitted as it is slow compared to H atom removal by ozone and *cis*-2-butene. The rate constants used to evaluate the relative importance of various reaction paths were the estimated or experimentally determined ones listed in the references given after each reaction. All the reactions postulated are exothermic and the observed mass numbers are consistent with the products expected from kinetic considerations.

The primary reaction step is assumed to involve the initial attack of ozone on the olefin.



$$CH_3CH{=}CHCH_3 + O_3 \longrightarrow \underset{\textstyle A}{CH_3\text{—}\overset{O-O-O}{CH\text{—}CH}\text{—}CH_3} \quad (1)$$

The *m/e* 104 peak may correspond to any of the structures shown in Table I. However, the hydroperoxide shown in reaction 2a is considered to be the



$$A \longrightarrow \underset{m/e\ 104}{CH_3\text{—}\overset{O}{\overset{\|}{C}}\text{—}\overset{OOH}{\overset{|}{C}H}\text{—}CH_3} \quad (2a)$$

most likely product for the following reasons.

(1) The concentration of the species increases linearly with time as shown in Figure 4, while the primary "molozonide" A is expected to show steady state kinetics. Application of simple RRK[28] theory to the initially formed 1,2,3-trioxolane (A) which is assumed to contain the 45 kcal/mol exothermicity[29] from reaction 1 predicts a lifetime of $\sim 10^{-11}$ sec under these experimental conditions.

(2) There is some infrared absorption evidence for production of the secondary ozonide in gas phase ozone–olefin reactions.[16, 18] Recent infrared studies in the condensed phase at low temperatures have shown that the secondary ozonides are major reaction products.[30] However, formation of the secondary ozonide must occur either by rearrangement of the initial ozone–olefin adduct or by recombination of the Criegee "zwitterion" ($CH_3\dot{C}HOO\cdot$) with aldehyde,[20] both of which seem unlikely under our room temperature, low pressure conditions.

This direct observation of an adduct or rearranged product from an ozone–olefin reaction with a half-life ≥ 0.2 sec may be related to previous experimental observations. For example, while highly speculative, such a species could be the phytotoxicant in ozone–olefin reactions which causes plant damage[31] and may be involved in the rapid oxidation of SO_2 reported by Cox and Penkett[17] in O_3–olefin–SO_2 systems.

Reaction steps 2b–e involve the decomposition of the intermediate A, formed in the primary step 1.

$$A \longrightarrow CH_3CHO + CH_2CO + H_2O \quad (2b)$$

$$\longrightarrow CH_3CHO + CH_3OH + CO \quad (2c)$$

$$\longrightarrow HCO + C_3H_7 + O_2 \quad (2d)$$

$$\longrightarrow C_2H_5 + CH_3CO + O_2 \quad (2e)$$

Although the products other than acetaldehyde in eq 2b and 2c can be rationalized on the basis of the decomposition of the Criegee "zwitterion" (or biradical in the gas phase), no direct evidence for its existence was found.

CH_3CO and C_3H_7 may be produced in reactions 2d and 2e. Both of these species are expected to react rapidly with O_2 (reactions 3 and 4),[32] giving rise to a

$$C_3H_7 + O_2 \longrightarrow C_3H_7O_2 \quad (3)$$

$$CH_3CO + O_2 \longrightarrow CH_3CO_3 \quad (4)$$

$$k \sim 4 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

mass peak at *m/e* 75, consistent with the observations in Table I. Similarly, C_2H_5 radicals, formed *via* reaction 2e would be expected to react with either O_2 or O_3.

$$C_2H_5 + O_2(+M) \longrightarrow C_2H_5O_2(+M)$$

$$k \sim 2.5 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}\ {}^{32} \quad (5)$$

$$C_2H_5 + O_3 \longrightarrow C_2H_5O + O_2 \quad (6)$$

C_2H_5 appears to attain a steady state slowly (Figure 3b) from which estimates of k_5 and k_6 can be obtained using the simplified kinetic expression, which assumes a constant rate of formation of the intermediates where C

$$C = B(1 - e^{-Rt})$$

= concentration of the intermediate, B = constant, and R = the rate loss of the intermediate which, in general, will be governed by reaction with O_2, O_3, or *cis*-2-butene. If C_2H_5 reacts only with O_2, $k_5 \sim 5 \times 10^5$ l. mol^{-1} sec^{-1}, or, if in the third order pressure region,[33] $k_5 \sim 5 \times 10^9$ l.^{2} mol^{-2} sec^{-1}. If C_2H_5 reacts only with O_3, then $k_6 \sim 2 \times 10^7$ l. mol^{-1} sec^{-1}. A possible explanation for the lack of agreement of k_5 with literature values is that C_2H_5 is not produced exclusively in reaction 2e but could also arise through a much more complex reaction sequence.

The reactions

$$HCO + O_2 \longrightarrow HO_2 + CO$$

$$k \sim 1 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}\ {}^{34} \quad (7)$$

$$HCO + O_3 \longrightarrow [HCO_2]^* + O_2 \longrightarrow H + CO_2 + O_2 \quad (8)$$

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[26] M. J. Kurylo, *J. Phys. Chem.*, 76, 3518 (1972), and references therein.

[27] D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions. Vol. 1: Homogeneous Gas Phase Reactions of the H_2–O_2 System," Butterworths, London, 1972.

[28] L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," Chemical Catalogue, New York, N. Y., 1932.

[29] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 173.

[30] L. A. Hull, I. C. Hisatsune, and J. Heicklen, *J. Amer. Chem. Soc.*, **94**, 4856 (1972).

[31] W. N. Arnold, *Int. J. Air Pollut.*, **2**, 167 (1959), and references therein.

[32] G. R. McMillan and J. G. Calvert, *Oxid. Combust. Rev.*, **1**, 83 (1965).

[33] N. Basco, D. G. L. James, and F. C. James, *Int. J. Chem. Kinet.*, **4**, 129 (1972).

[34] K. L. Demerjian, J. A. Kerr, and J. G. Calvert, *Advan. Environ. Sci. Technol.*, **4** (1973).

are expected to be the main removal processes for the HCO radical. While reaction 8 has not been experimentally verified, it may be one of the H atom sources responsible for the production of the Meinel band emission of the OH radical.[1] In this work, the very rapid rise of HCO to a steady state concentration means that only lower limits of the rate constants for reactions 7 and 8 can be obtained. If HCO reacts only with O_2, then $k_7 \geq 1 \times 10^7$ l. mol^{-1} sec^{-1}, or, if it reacts only with O_3, then $k_8 \geq 5 \times 10^8$ l. mol^{-1} sec^{-1}.

From previous investigations, the reactions of HO_2,[34–36] H,[6–8, 37–39] and OH[40–44] expected in the present experimental system are given by reactions 9–16.

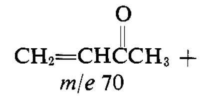
$$HO_2 + CH_3CH{=}CHCH_3 \longrightarrow \underset{m/e\ 89}{CH_3CH(O_2H)\dot{C}HCH_3}$$

$$k \sim 3.3 \times 10^6 \text{ l. mol}^{-1}\text{ sec}^{-1\ 34,35} \quad (9)$$

$$CH_3CH(O_2H)\dot{C}HCH_3 + CH_3CH{=}CHCH_3 \longrightarrow$$

$$\underset{m/e\ 90}{CH_3CH(OOH)CH_2CH_3} + \cdot CH_2CH{=}CHCH_3 \quad (10a)$$

$$\cdot CH_2CH{=}CHCH_3 \longleftrightarrow CH_2{=}CH\dot{C}HCH_3 \xrightarrow{O_2}$$



$$\underset{m/e\ 70}{CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_3} + OH \quad (10b)$$

$$HO_2 \longrightarrow \text{Wall} \quad (11)$$

$$H + O_3 \longrightarrow OH_{\nu}\dagger_{\leq 9} + O_2$$

$$k = 1.6 \times 10^{10} \text{ l. mol}^{-1}\text{ sec}^{-1\ 6-8} \quad (12)$$

$$OH_{\nu}\dagger_{\leq 9} \longrightarrow OH + h\nu \text{ (Meinel bands)}$$

$$k = 3.4\text{–}16 \text{ sec}^{-1\ 40} \quad (13)$$

$$\begin{aligned} OH_{\nu}\dagger_{\leq 9} + O_3 &\longrightarrow HO_2 + O_2 \\ &\longrightarrow O + O_2 + OH \quad (14) \\ &\longrightarrow H + 2O_2 \end{aligned}$$

$$k = 1.2 \times 10^8\ (\nu = 0) \text{ to } 5 \times 10^9\ (\nu = 9) \text{ l. mol}^{-1}\text{ sec}^{-1\ 36,40}$$

$$OH + CH_3CH{=}CHCH_3 \longrightarrow$$

$$\underset{m/e\ 73}{CH_3CH(OH)\dot{C}HCH_3} \longrightarrow \underset{m/e\ 72}{CH_3COC_2H_5}$$

$$k = 3.7 \times 10^{10} \text{ l. mol}^{-1}\text{ sec}^{-1\ 41,42} \quad (15)$$

$$H + CH_3CH{=}CHCH_3 \longrightarrow C_4H_9{}^*$$

$$k = 5 \times 10^8 \text{ l. mol}^{-1}\text{ sec}^{-1\ 37-39} \quad (16)$$

For HO_2, reaction with O_3 is unimportant ($k = 1.8 \times 10^6$ l. mol^{-1} sec^{-1}),[36] and thus assuming HO_2 reacts with *cis*-2-butene, k_9 can be estimated from the rise of HO_2 to its steady state to be approximately 1×10^7 l. mol^{-1} sec^{-1}, which is consistent with literature estimates.[34,35]

Morris and Niki[42] have determined by time of flight mass spectrometry that at least part of the reaction of OH radicals with *cis*-2-butene proceeds by addition; transient mass peaks were observed corresponding to the OH–olefin adduct. Also, by analogy with the products observed by Morris, *et al.*,[41] for OH + C_2H_4, C_3H_6, it is expected that methyl ethyl ketone will be the major stable product in the case of OH + *cis*-2-butene.

The vibrationally excited C_4H_9 radical can undergo reactions 17a and 17b in the present system.[45] The

$$C_4H_9{}^* + M \longrightarrow C_4H_9 + M \quad (17a)$$

$$C_4H_9{}^* \longrightarrow CH_3 + C_3H_6 \quad (17b)$$

CH_3 produced in reaction 17b can react with either oxygen or ozone.

$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$$

$$k \sim 10^{11} \text{ l.}^2\text{ mol}^{-2}\text{ sec}^{-1\ 33} \quad (18)$$

$$\begin{aligned} CH_3 + O_3 &\xrightarrow{a} CH_3O + O_2 \\ &\xrightarrow{b} HCHO + HO_2 \end{aligned}$$

$$k \sim 10^{10} \text{ l. mol}^{-1}\text{ sec}^{-1\ 14,46} \quad (19)$$

If reactions 16–19 become important at longer reaction times, the anomalous rise in CH_3O_2 (*m/e* 47) at longer reaction times may be explained; however, fragmentation in the mass spectrometer to produce CH_3O_2 cannot be excluded at this time.

This latter possibility is supported by the fact that, although reaction 17b is postulated as the source of CH_3 in this system, substantial quantities of C_3H_6 were not observed.

In similar manner, stabilized C_4H_9 radicals are expected to react with O_2 and O_3.

$$C_4H_9 + O_2 \longrightarrow \underset{m/e\ 89}{C_4H_9O_2} \quad (20)$$

$$C_4H_9 + O_3 \longrightarrow \underset{m/e\ 73}{C_4H_9O} + O_2 \quad (21)$$

The results of this study do not permit detailed formulation of a reaction scheme for the ethylene and isobutene oxidations. The observed major stable products are expected to arise from the decomposition of the initial ozone–olefin adduct.

While the mechanism presented for the *cis*-2-butene–ozone reaction is obviously tentative and incomplete, the observation of radical species, such as HCO and HO_2, provides evidence for alternative reaction pathways to the Criegee mechanism which has previously been applied. Thus, while more detailed investigations using a wide variety of olefins are obviously needed, this study provides the first conclusive experimental evidence for the involvement of radicals in gas phase ozone–olefin reactions.

Acknowledgment. The authors are grateful to Professor K. D. Bayes of UCLA for making the equipment used in this study available and for his interest and suggestions during the course of this work. The authors also wish to thank Professor J. G. Calvert, Dr. W. B. DeMore, Dr. H. Niki, and Dr. A. C. Lloyd for making preprints of their work available before publication and are appreciative of helpful comments from Dr. Lloyd during the preparation of this manuscript. This project has been financed in part with funds from the Office of Naval Research, Contract

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(35) A. C. Lloyd, "Estimated and Evaluated Kinetic Data for Gas Phase Reactions of the Hydroperoxyl Radical," National Bureau of Standards Report 10447, July 1971; *Int. J. Chem. Kin.*, submitted for publication.

(36) W. B. DeMore, *Science*, **180**, 735 (1973).

(37) E. E. Daby and H. Niki, *J. Chem. Phys.*, **51**, 1255 (1969).

(38) J. A. Cowfer, D. G. Keil, J. V. Michael, and C. Yeh, *J. Phys. Chem.*, **75**, 1584 (1971).

(39) E. E. Daby, H. Niki, and B. Weinstock, *J. Phys. Chem.*, **75**, 1601 (1971).

(40) R. N. Coltharp, S. D. Worley, and A. E. Potter, *Appl. Opt.*, **10**, 1786 (1971).

(41) E. D. Morris, Jr., D. H. Stedman, and H. Niki, *J. Amer. Chem. Soc.*, **93**, 3570 (1971).

(42) E. D. Morris, Jr., and H. Niki, *J. Phys. Chem.*, **75**, 3640 (1971).

(43) D. D. Drysdale and A. C. Lloyd, *Oxid. Combust. Rev.*, **4**, 157 (1970).

(44) W. E. Wilson, Jr., *J. Phys. Chem. Ref. Data*, **1**, 535 (1972).

(45) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(46) J. G. Calvert and P. L. Hanst, *Can. J. Chem.*, **37**, 1671 (1959).

N00014-69A-0200-500, partly from Federal funds from the Environmental Protection Agency under Grant No. 800649 and partly from NSF Grant GP-34524. The contents do not necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. One of the authors (B. J. F.) is grateful for support on an Intercampus Research Opportunity Fund grant during the course of this work. The construction and operation of the photoionization mass spectrometer was supported by the Environmental Protection Agency, Grant R801395, and the Air Force Office of Scientific Research, Grant AFOSR-70-1872.

Absorption and Emission Spectroscopy of Pyruvic Acids and Pyruvate Esters

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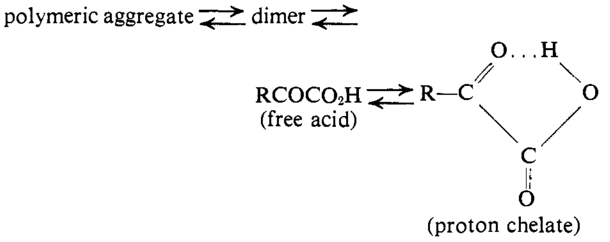
Abstract: The absorption and emission properties of pyruvic and trimethylpyruvic acid and their methyl esters have been investigated. Solutions of both α-keto acids are characterized by complex equilibria between monomeric and aggregated species which, individually, sample a varied geometric population. The spectroscopy of these compounds is a consequence of these equilibria. Absorption studies show that *all* entities in solutions of both acids and esters exist to some extent in a planar dicarbonyl geometry although the *preferred* geometry may be severely twisted. It is suggested that the relaxed emitting triplet possesses a planar dicarbonyl geometry with the energy of the emissions being a function of both solute–solute and solute–solvent interactions. Multiple emissions are observed at 77°K for both the keto acids in dilute 3-methylpentane glasses as well as in hydrogen-bonding glasses. Methyl trimethylpyruvate in a 3-methylpentane glass also exhibits multiple emissions which are attributed to variously aggregated species presumably bonded through dipole–dipole interactions. All observed luminescences are assigned as $^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$.

Despite extensive interest[1] in the biological and photochemical properties of α-keto acids, the absorption and luminescence characteristics of these compounds are neither well understood nor much investigated. Extensive infrared and cryoscopic studies[2] have indicated that solutions of α-keto acids are best described by the following equilibria.



(1)

Although the absorption spectra of dilute solutions of aliphatic α-keto acids have been described[3] in terms of the free and chelated acid, the effects of concentration and temperature on the observed absorptions are unexplored. No discussion of the absorption properties of aliphatic α-keto esters is extant. Such luminescence data[1,4] as are available are fragmentary at best, consisting of little more than the observation that luminescence is observed in rigid media at 77°K. In short, the consequences of the monomer–aggregate equilibria on the spectroscopic properties of solutions of α-keto acids have not been considered. Consequently, the emission and absorption characteristics of the following compounds have been investigated: pyruvic acid (PA), methyl pyruvate (MP), trimethylpyruvic acid (TMPA), and methyl trimethylpyruvate (MTMP).

Experimental Section

PA (Aldrich) and MP (Eastman) were obtained commercially. TMPA and MTMP were prepared by the method of Richard.[5] All compounds were repeatedly vacuum distilled prior to use and their purity confirmed by gas chromatography. All solvents employed were nonemissive in the region of experimental interest. Films were prepared by placing several drops of the compound between two quartz plates and rapidly cooling to 77°K. The polycrystalline film thus obtained had suitable optical properties for absorption and emission studies. Instrumentation and other techniques have been described previously.[6]

Prolonged irradiation of 10^{-3} *M* solutions in either EPA (*i.e.*, ether–isopentane–alcohol mixture) or 3-MP (*i.e.*, 3-methylpentane) with the full output of a G.E. AH-6 mercury arc lamp, both at ambient temperature and 77°K, did not alter the 77°K emission profiles. This fact indicates that the emissions observed are intrinsic to the keto acid systems and do not arise from photoproducts. Moreover, the known photoproducts[1,4] from the irradiation of PA and MP are nonemissive in the region of experimental interest. Esterification, by the addition of diazomethane, of a 3-MP solution of TMPA which exhibits multiple luminescences leads to the observation of the emission profile characteristic of MTMP

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[1] (a) M. B. Rubin, *Fortschr. Chem. Forsch.*, **31**, 251 (1969); (b) B. M. Monroe, "Advances in Photochemistry," Vol. 8, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Wiley-Interscience, New York, N. Y., 1971, pp 77–108.

[2] (a) L. Oehme and A. Schellenberger, *Chem. Ber.*, **101**, 1499 (1968); (b) A. Schellenberger and L. Oehme, *Z. Phys. Chem.* (*Leipzig*), **227**, 112 (1964).

[3] G. Fischer, L. Oehme, and A. Schellenberger, *Tetrahedron*, **27**, 5683 (1971).

[4] (a) P. A. Leermakers and G. F. Verley, *J. Amer. Chem. Soc.*, **85**, 3776 (1963); (b) P. A. Leermakers, P. C. Warren, and G. F. Verley, *ibid.*, **86**, 1768 (1964).

[5] A. Richard, *Ann. Chim.* (*Paris*), **21**, 360 (1910).

[6] D. B. Larson and S. P. McGlynn, *J. Mol. Spectrosc.*, submitted for publication.

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