REACTION OF OXYGEN ATOMS WITH ACETALDEHYDE[1]

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ABSTRACT

Reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with acetaldehyde has been studied at room temperature. The major products of the reaction are water and biacetyl and the only primary process appears to be

$$CH_3CHO + O \rightarrow \dot{C}H_3CO + OH \qquad [1]$$

followed by

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O \qquad [2]$$

and

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2. \qquad [3]$$

At room temperature oxygen atoms react with acetaldehyde 0.7 ± 0.1 times as fast as with ethylene, so that the activation energy of reaction [1] is likely to be close to 3 kcal./mole.

INTRODUCTION

The present work is the second in a series of investigations of the reactions of oxygen atoms with different organic compounds. In a previous publication (6) the reaction of oxygen atoms with ethylene has been described.

Oxygen atoms are produced by mercury photosensitized decomposition of nitrous oxide. It has been shown (7) that the primary step in this reaction is the formation of an atom of oxygen and a molecule of nitrogen and the rate of nitrogen production serves as a measure of oxygen atoms participating in the process. The important advantage of the use of nitrous oxide, in addition to the presence of an internal actinometer, is the absence of molecular oxygen, which by its rapid reaction with free radicals normally obscures the primary reactions of the atoms.

The reaction of oxygen atoms with acetaldehyde is of considerable interest, particularly in view of its possible participation in the process of oxidation of this compound (2, 3, 12, 13). Avramenko and Lorentso (2, 3) made an attempt to study this reaction directly, by generating oxygen atoms in O_2 and, alternatively, in H_2O. In the former case the mixture from the discharge contained O and O_2, and in the latter case it presumably contained H, O, some OH, the excess H_2O, but almost no O_2. The experiments were performed at 100° C. and the following products were observed: HCHO, CO, CO_2, organic hydroperoxides, CH_3COOH, and some HCOOH. With the H_2O discharge CH_4 and C_2H_4 were also formed. In view of the diversity of the products formed and on the basis of similar experiments with formaldehyde, these authors postulated a variety of primary steps

$$O + CH_3CHO \rightarrow CO_2 + CH_3 + H \qquad [4a]$$

$$\rightarrow CHO + HCHO + H \qquad [4b]$$

$$\rightarrow CH_3COOH \qquad [5]$$

and came to the conclusion that $k_4 > k_5 > k_1$, i.e. that the abstraction of a

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[1] *Manuscript received January 26, 1956.*
Contribution from the Divison of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3953.

single atom of hydrogen was the least probable of the primary processes believed to occur.

The properties ascribed to oxygen atoms by Avramenko and Lorentso are radically different from those usually assumed, notably by Geib (10) who investigated the reaction of oxygen atoms with formaldehyde. Direct experimental evidence, however, is quite scant and in the case of acetaldehyde the paper of Avramenko and Lorentso appears to be the only published work. For this reason the reaction of oxygen atoms, produced by mercury photosensitized decomposition of nitrous oxide, with acetaldehyde has been studied with the object of establishing the primary process and of obtaining some information about the rate of the reaction.

EXPERIMENTAL

The experimental arrangement has been described in detail previously (6). Acetaldehyde was a Matheson Co. product used after thorough degassing and bulb to bulb distillation *in vacuo*.

The products condensable in liquid nitrogen were fractionated on a Le Roy still (11). The "liquid products" were fractionated on a gas–liquid partition chromatographic column (5). Use has also been made of mass-spectroscopic and infrared analysis.

Quantum yields were determined relative to the rate of hydrogen production from 200 mm. of butane at 25° for which Bywater and Steacie (4) find a quantum yield of 0.50. Allowance for a slight drift in the intensity of the incident resonance radiation was made by its frequent determination and interpolation for individual runs.

RESULTS AND DISCUSSION

Relative Quenching Efficiency of Acetaldehyde

In order to establish the suitable range of experimental conditions for the study of the reaction of oxygen atoms with acetaldehyde, it was necessary first to determine the relative quenching efficiency of nitrous oxide and acetaldehyde and the products resulting from the direct mercury sensitized decomposition of the latter compound. The results of experiments with 100 mm. of nitrous oxide and varying amounts of acetaldehyde are given in Table I. Considering for the moment only the series A in Table I, it is seen that with increasing acetaldehyde the quantum yield of nitrogen (ϕ_{N_2}) decreases while the yields of the other observed products relative to R_{N_2}, i.e., to the rate of introduction of oxygen atoms into the process, increase. (With larger amounts of acetaldehyde used in this series of experiments no attempt was made to analyze for such less volatile products as water, biacetyl, or acetone.) The trend in ϕ_{N_2} is due to the competition by the two reactants for the Hg $6(^3P_1)$ atoms and the plot of $1/\phi_{N_2}$ against the acetaldehyde to nitrous oxide ratio can be used in the manner described in an earlier publication (8) to determine the relative over-all quenching efficiency of the two compounds. The plot is given in Fig. 1 and the ratio of the slope to the intercept, i.e., the

TABLE I

MERCURY PHOTOSENSITIZED DECOMPOSITION OF MIXTURES OF 100 MM. OF NITROUS OXIDE AND VARYING AMOUNTS OF ACETALDEHYDE

Run	CH_3CHO, mm.	N_2O, mm.	ϕ_{N_2}	Relative yields of products ($R_{N_2} = 1$) CO	H_2	CH_4	C_2H_6	r.t.*	H_2O	$(CH_3CO)_2$	CH_3COCH_3	$-\Delta CH_3CHO$
Series A. Exposure 90 min., mean I_a = 3.18×10¹⁵ quanta sec.⁻¹, 23±1°C.												
36	127.6	98.9	0.202	1.50	0.321	1.05	0.223					
34	101.0	100.9	0.238	1.21	0.264	0.775	0.203					
37	68.1	100.4	0.311	0.803	0.180	0.422	0.140					
33	42.5	99.9	0.397	0.509	0.121	0.229						
35	20.5	101.3	0.539	0.254	0.040	0.074	0.019					
Series B. Exposure 120 min., mean I_a = 2.59×10¹⁵ quanta sec.⁻¹, 25±1°C.												
56	15.7	100.3	0.572	0.201	0.044	0.050		1.39	1.0	0.4	0.14	3.3
58	4.92	100.4	0.660	0.110	0.019	0.014	0.010	1.42	0.8	0.7	0.10	2.1
60	3.67	100.2	0.667	0.107	0.017	0.010		1.39				1.7
59	3.66	100.6	0.663	0.109	0.012	0.010		1.20				
57	2.52	100.5	0.728	0.141	0.018	0.011	None	1.03	0.6	0.4	0.07	1.4

**r.t. = room temperature fraction.*

ratio of the over-all quenching efficiency of acetaldehyde to that of nitrous oxide, is 2.28. This value leads to the previously reported (8) relative quenching cross section of acetaldehyde.

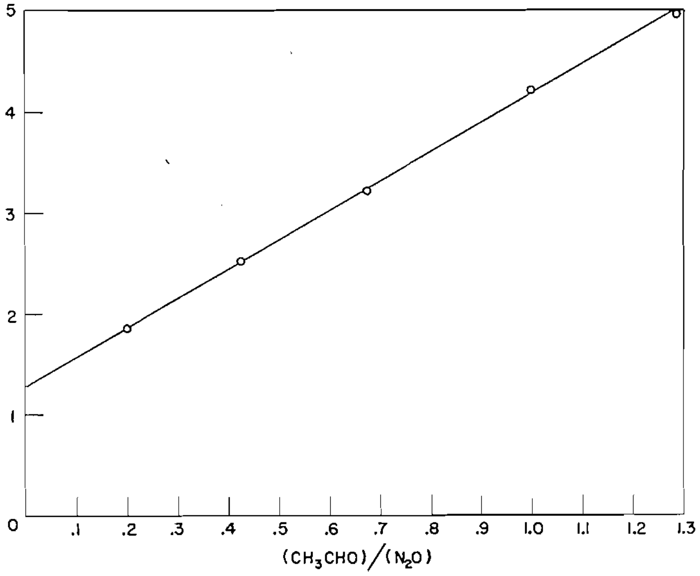

FIG. 1. Plot of the reciprocal quantum yield of nitrogen against $(CH_3CHO)/(N_2O)$ ratio. (100 mm. of N_2O, 23±1°C., mean I_a 3.18×10^{15} quanta/sec., irradiation 90 min.)

Reaction of Oxygen Atoms with Acetaldehyde

The large quenching efficiency of acetaldehyde necessitates small acetaldehyde to nitrous oxide ratios in the study of the reaction of oxygen atoms. At the same time at too small acetaldehyde pressures there is possibility of secondary reactions of oxygen atoms with the products formed. Fig. 2 shows a plot of the relative rates of formation of the more volatile products per oxygen atom introduced into the process against the CH_3CHO to N_2O ratio. For Series A the rates of formation of CO, CH_4, H_2, and C_2H_6 extrapolate to zero as the CH_3CHO to N_2O ratio approaches zero, indicating that these

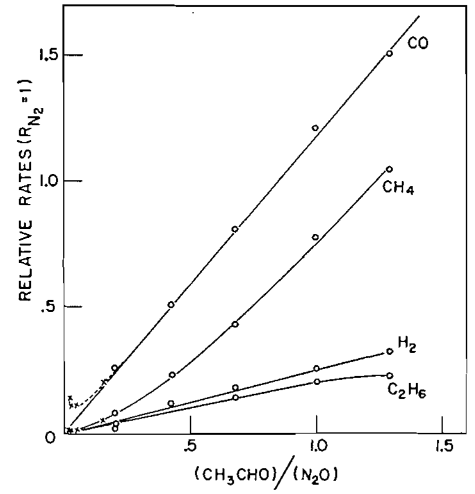

FIG. 2. Relative yields in the mercury photosensitized decomposition of 100 mm. of N_2O and varying amounts of CH_3CHO. Open circles refer to Series A and crosses to Series B, Table I.

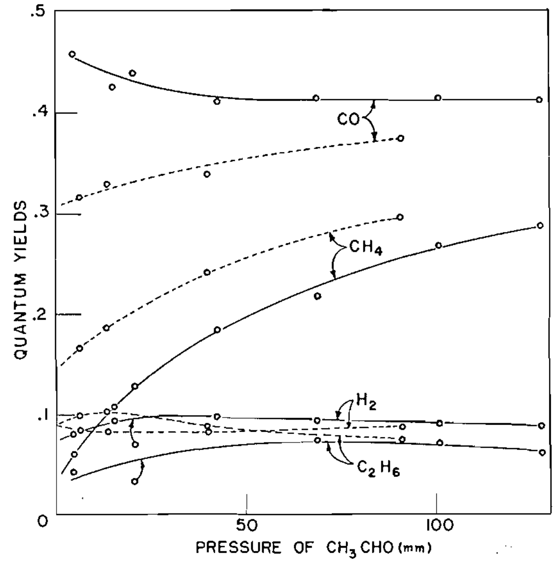

FIG. 3. Quantum yields of gaseous products in the mercury photosensitized decomposition of CH_3CHO alone (broken lines) and of its mixtures with N_2O (continuous lines) as a function of the partial pressure of CH_3CHO.

compounds are due to quenching by acetaldehyde and not to the reaction of oxygen atoms. A few experiments with acetaldehyde alone showed that the same products were formed in the direct mercury sensitized decomposition of this compound. The results are given in Fig. 3 and it is seen that the quantum yields of these products approach at high acetaldehyde pressure those obtained from the mixtures of acetaldehyde and nitrous oxide.* The reasons for the differences at lower acetaldehyde pressures will be discussed after the primary reaction of oxygen atoms with acetaldehyde has been considered.

The results of a number of experiments with lower initial acetaldehyde pressures are given in Table I, Series B. In these experiments it was possible to isolate on the Le Roy still the acetaldehyde fraction (at −80° C.) and subsequently the residual "room temperature" fraction. Both these fractions were analyzed by gas–liquid partition chromatography and by mass-spectrometric methods. The former was found to contain in addition to the unreacted acetaldehyde appreciable amounts of acetone, and the latter large amounts of biacetyl and water. These compounds were not found in the mercury sensitized decomposition of acetaldehyde alone. No other compounds were detected and, in particular, mass spectrometer analysis of the "room temperature" fraction showed absence of acetic acid and alcohols.

The formation of biacetyl and water as the major products under the conditions of the series B of experiments indicates that the following reactions occur:

$$CH_3CHO + O \rightarrow CH_3CO + OH, \quad [1]$$

$$CH_3CHO + OH \rightarrow CH_3CO + H_2O, \quad [2]$$

$$CH_3CO + CH_3CO \rightarrow (CH_3CO)_2. \quad [3]$$

In the absence of any other reactions, the relative rates per oxygen atom would be for water and biacetyl unity and for the consumption of acetaldehyde two. Several other reactions involving CH_3CO radicals must, however, be also considered. Since a certain amount of direct quenching by acetaldehyde occurs even in the experiments where quite small quantities of this compound are used, methyl radicals are also present and their combination with CH_3CO explains the formation of some acetone. Ausloos and Steacie (1) have suggested also abstraction of hydrogen from CH_3CO by CH_3 radicals and disproportionation of two CH_3CO radicals to form ketene and acetaldehyde. In view of this, the relative yield of biacetyl will be lower than unity as a result of the reactions

$$CH_3CO + CH_3 \rightarrow CH_3COCH_3, \quad [6]$$

$$CH_3CO + CH_3 \rightarrow CH_4 + CH_2CO, \quad [7]$$

$$CH_3CO + CH_3CO \rightarrow CH_3CHO + CH_2CO, \quad [8]$$

and possibly to a small extent also

$$CH_3CO \rightarrow CH_3 + CO. \quad [9]$$

At very small acetaldehyde pressures, on the other hand, there is also the possibility of incomplete utilization of O-atoms in reaction [1] and of OH

**The latter quantum yields were calculated relative to the fraction of the incident radiation quenched by acetaldehyde.*

radicals in reaction [2] because of their reactions with the compounds or free radicals formed.* As the acetaldehyde pressure becomes larger the relative yield of biacetyl would be expected to increase and, after reaching a maximum value smaller than unity, to start to decrease again because of the increasing importance of reactions [6] and [7]. The trends in the yields of biacetyl, water, and acetone, and in the consumption of acetaldehyde in the series B of experiments, Table I, are in agreement with these interpretations, although lack of knowledge of the rate constants of the reactions involved and the considerable difficulty of accurately analyzing for these products preclude a detailed quantitative treatment. With the huge amounts of nitrous oxide used no attempt was made to analyze for ketene.

The deviations in Fig. 3 at lower acetaldehyde pressures of the quantum yields of the products resulting from direct quenching by acetaldehyde alone and in the presence of nitrous oxide are understandable in view of the occurrence of reactions [6] to [9]. Methyl radicals are undoubtedly a primary product of the mercury sensitized decomposition of acetaldehyde. Acetyl radicals, on the other hand, appear to be produced in the studied process only by the action of oxygen atoms and then, as a result of reactions [6] and [7], lead to a decrease in CH_3 radical concentration and, therefore, also to a smaller production of methane and ethane (by abstraction and recombination, respectively). The somewhat increased formation of carbon monoxide in the presence of oxygen atoms may be due to some occurrence of reaction [9] and to secondary processes. An evidence for the latter is found in the results given in Table II for a series of experiments with 100 mm. N_2O and 3.6 mm. CH_3CHO irradiated for different lengths of time. There is a distinct increase in the relative yield of carbon monoxide with increasing reaction time. The extrapolated initial yields, after allowing for the direct quenching by acetaldehyde, are quite small.

TABLE II

THE EFFECT OF REACTION TIME ON THE RELATIVE YIELDS OF GASEOUS PRODUCT PER OXYGEN ATOM CONSUMED

(Mean I_a 1.76×10^{15} quanta/sec., 100 mm. N_2O and 3.6 mm. CH_3CHO)

Run	Temp., °C.	Irradn., min.	ϕ_{N_2}	Relative yields ($R_{N_2} = 1$)		
				CO	H_2	CH_4
24	25.3	60	0.64	0.109	0.014	0.011
25	26.2	120	0.65	0.111	0.006	0.017
18	26.9	180	0.64	0.121	0.013	0.007
26	25.7	240	0.66	0.130	0.016	0.009
23	25.1	300	0.65	0.147	0.021	0.009

**Various reactions of this type could be suggested, for example those of O-atoms or OH radicals between themselves or with acetyl radicals, leading perhaps in the latter case to the formation of acetic acid. No acetic acid, however, is detected in the product. Although it could be argued that this compound might undergo further attacks once it is formed, postulates of this kind would be very speculative in the absence of any supporting evidence. At present it would seem better not to attempt to specify these processes in any detail. Their net effect, as well as of possible analogous reactions involving the products, must be a decrease in the yields of biacetyl and water at very small acetaldehyde pressures.*

The present experiments indicate that the only mode of reaction of oxygen atoms with acetaldehyde is the abstraction of the aldehydic hydrogen atom to give an OH and a CH_3CO radical. This result is in disagreement with the postulates of Avramenko and Lorentso (2, 3), who consider the abstraction of the hydrogen atom to be the least probable of the assumed several distinct modes of primary reaction. It ought to be pointed out, however, that the experiments of these authors were conducted at a higher temperature where CH_3CO radicals are known to decompose readily. A further complicating feature might have been the presence of relatively large concentrations of hydrogen atoms and possibly also of some molecular oxygen even in the H_2O discharge.

Estimate of the Activation Energy of the Reaction

In order to obtain information on the rate of the reaction of oxygen atoms with acetaldehyde, several experiments were conducted at 25° C. with mixtures of 300 mm. of N_2O and varying ratios of smaller amounts of CH_3CHO and C_2H_4. To minimize any depletions of the reactants in the course of the reaction a circulating system of total volume 500 ml. was employed. The results are given in Table III. Direct quenching by C_2H_4 resulted, at the high total pressures used, in essentially complete collisional deactivation. The processes to be considered in addition to reactions [1] and [2] are

TABLE III

EXPERIMENTS WITH MIXTURES OF 300 MM. OF N_2O AND VARYING AMOUNTS OF CH_3CHO AND C_2H_4 (25±1°C., CIRCULATING SYSTEM)

Run	CH_3CHO, mm.	C_2H_4, mm.	$\frac{CH_3CHO}{C_2H_4}$	Irradn., min.	R_{N_2}, molec.cc.$^{-3}$ sec.$^{-1}$ $\times 10^{-15}$	Relative rates (R_{N_2} = 1)			
						CO	CH_4	H_2	$-\Delta C_2H_4$
73	—	51.3	—	65	1.23	0.471	0.146	0.078	
72	4.83	51.6	0.094	60	1.21	0.448	0.143	0.095	
71	5.15	19.9	0.259	60	1.42	0.404	0.125	0.072	
70	4.90	9.94	0.493	60	1.49	0.378	0.117	0.064	0.917
69	4.73	4.94	0.961	60	1.51	0.332	0.106	0.068	
76	2.44	1.06	2.30	60	1.69	0.251	0.048	0.059	0.484
78	4.90	1.06	4.64	60	1.63	0.244	0.040	0.043	0.280
79	7.92	1.06	7.49	60	1.71	0.185	0.036	0.040	
81	8.03	1.06	7.61	120	1.79	0.189	0.035	0.041	0.190
75	4.74	0.524	9.05	60	1.64	0.179	0.030	0.043	
74	4.82	—	∞	60	1.63	0.126	0.010	0.002	—

NOTE: *the R_{N_2} values are not strictly comparable between themselves since the reaction cell was occasionally flamed and the transparency of the front window fluctuated to some extent. Mean I_a remained about 2.3$\times$10^{15} quanta/sec.*

$$C_2H_4 + O \rightarrow \text{Products} \qquad [10]$$

and

$$C_2H_4 + OH \rightarrow \text{Products.} \qquad [11]$$

The products of reaction [10] are known (6, 9), while no information on reaction [11] appears to be available. It will be assumed, subject to subsequent justification, that reaction [11] cannot compete successfully with reaction [2] for OH radicals under the conditions of the experiments performed. It is then possible to evaluate k_1/k_{10} by comparing the relative rates of formation of different products or of the consumption of the reactants as CH_3CHO to C_2H_4 ratio is varied, since it was found that this ratio remained virtually unaltered in the course of reaction with the amounts and conversion levels used. Thus, in the reaction of oxygen atoms with about 1 mm. ethylene in the presence of 300 mm. N_2O the relative rate of over-all consumption of ethylene per oxygen atom is about 1.2. If in the mixtures of C_2H_4 and CH_3CHO the latter compound does not interfere with the reaction of O-atoms with ethylene except by using some of the available O-atoms, the following relationship would be expected to hold

$$\frac{R_{N_2}}{R_{C_2H_4}} = 1.2\left(1 + \frac{k_1}{k_{10}}\,\frac{(CH_3CHO)}{(C_2H_4)}\right).$$

The plot of $R_{N_2}/R_{C_2H_4}$ vs. $(CH_3CHO)/(C_2H_4)$ is given in Fig. 4 and the value of k_1/k_{10} obtained from the slope to intercept ratio is 0.68. In a similar manner, if any one of the relative rates per oxygen atom ($\zeta = R/R_{N_2}$) has a value α with C_2H_4 alone and β with CH_3CHO alone, then

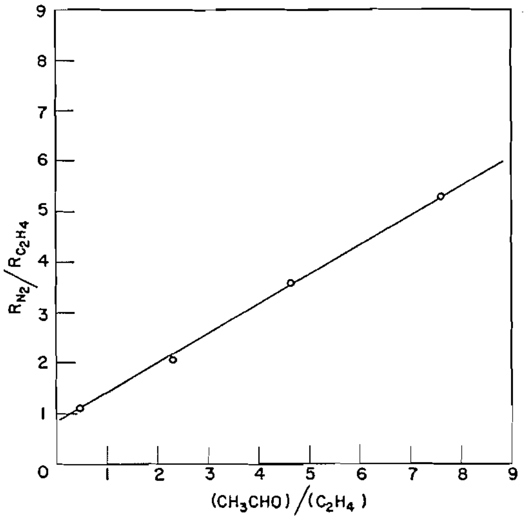

FIG. 4. Plot of the reciprocal rate of C_2H_4 consumption per oxygen atom vs. $(CH_3CHO)/(C_2H_4)$ ratio.

$$\epsilon = \frac{\zeta-\alpha}{\beta-\zeta} = \frac{k_1}{k_{10}}\,\frac{(CH_3CHO)}{(C_2H_4)}.$$

In Fig. 5 are given the plots of ϵ against $(CH_3CHO)/(C_2H_4)$ for CO and CH_4 with the respective α and β values as found experimentally in runs 73 and 74 (Table III). There is a considerable scatter of points, which is readily explainable by limitations in analytical accuracy. A corresponding plot for the relatively small H_2 production is for the same reason much too uncertain, although the trend is qualitatively the same. The results for CO and CH_4 are mutually in reasonably good agreement and the slope of what appears to be the best line through the points gives 0.64 as the value of k_1/k_{10}.

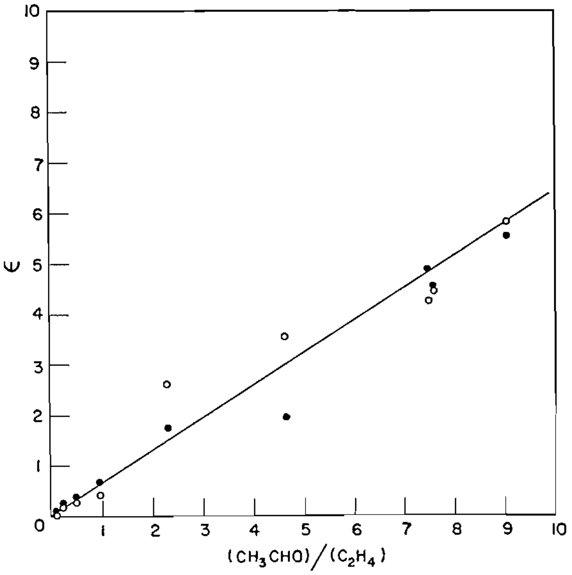

FIG. 5. Plots of ϵ_{CH_4} (open circles) and ϵ_{CO} (filled circles) vs. $(CH_3CHO)/(C_2H_4)$ ratio.

The value of k_1/k_{10} can also be estimated by comparing the rates of consumption of the two reactants. If the over-all consumption of C_2H_4 per oxygen atom is about 1.2 and that of CH_3CHO is presumably 2, the following relationship would be expected to hold

$$\frac{k_1}{k_{10}} = \frac{1.2}{2}\,\frac{(C_2H_4)}{(CH_3CHO)}\,\frac{R_{CH_3CHO}}{R_{C_2H_4}}\,.$$

It is difficult to determine accurately the rate of CH_3CHO consumption, in particular since some aldehydes are a product of the reaction of O-atoms with C_2H_4 (6). However, by applying reasonable corrections the values of R_{CH_3CHO} in addition to the corresponding $R_{C_2H_4}$ were obtained for two runs. In both cases k_1/k_{10} was thus found to be somewhat larger than 0.6 with probable uncertainty not greater than about 20%.

The values of k_1/k_{10} obtained in different ways are therefore mutually consistent and it appears reasonably certain that at room temperature $k_1/k_{10} = 0.7 \pm 0.1$. In view of this it is likely that E_1 is close to 3 kcal./mole, the value recently estimated (6) for reaction [10]. The work now in progress with a number of olefinic hydrocarbons with the use of improved analytical techniques (5) may provide means for additional verification of these values and for eventual determination of the activation energy differences for a number of reactions of oxygen atoms with common organic compounds.

The consistency of the k_1/k_{10} values obtained in different ways provides justification for the earlier made assumption that OH radicals react preferentially with acetaldehyde. The alternative assumption that in the performed experiments oxygen atoms reacted exclusively with CH_3CHO and that the observed trends were due to a competition for OH radicals rather than for O-atoms is highly unlikely. This assumption would require that OH radicals form with ethylene the same type of products and moreover in the same ratio as are formed in the interaction of oxygen atoms with ethylene. The results in Table III show that the yields of CO, CH_4, and H_2 approach those obtained with C_2H_4 alone as the $(CH_3CHO)/(C_2H_4)$ ratio approaches zero and in the reaction of O-atoms with C_2H_4 no OH radicals are formed.

ACKNOWLEDGMENT

The author is indebted to Mr. L. C. Doyle for assistance in the experimental work reported, to Dr. A. B. Callear for several gas chromatographic determinations, and to Dr. A. Tickner for mass-spectrometer analyses.

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