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means that $\frac{1}{2}NW(0)$, the static lattice potential, is also calculated (theoretically) exactly. The rejection of the nonadditivity contribution cannot, then, be regarded as arising through some compensating factor in the calculation of λ_0 and $W(0)$. The interpretation of solid-state zero-point properties is often made by calculating the static lattice potential using virial coefficient parameters and using the $\frac{9}{8}R\theta_D$ zero-point contribution. This can only be regarded as valid, and hence any further conclusions based on this as to nonadditivity can only be regarded as valid, if the parameter values are also shown to give a zero-point energy in agreement with the $\frac{9}{8}R\theta_D$ value.

CONCLUSIONS

From the calculations reported in these three papers we conclude that the 12:6 pair-potential, though largely empirical, gives a satisfactory account of the solid-state thermodynamic properties of the inert gases. Nonadditivity corrections appear unwarranted within the compass of the present theory. The use of the 12:6 potential in calculations relating to the liquid state would appear valid, particularly in view of the many other theoretical difficulties met with in making such calculations. We further feel that in view of the empirical nature of any pair-potential the second virial coefficient is a far too insensitive and indecisive a property to characterize the reduction parameters. The greater sensitivity of the zero-point crystal properties and the unique value obtained by their consideration make them much more suitable for such characterization.

ACKNOWLEDGMENTS

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Reaction of Oxygen Atoms with Acetaldehyde*

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The reaction of the ground-state triplet oxygen atoms with acetaldehyde at room temperature has been reinvestigated. Two different sources of oxygen atoms have been used: mercury photosensitized decomposition of nitrous oxide and photolysis of nitrogen dioxide at 3660 Å. The results confirm the earlier conclusion from this Laboratory that the primary attack involves the abstraction of the aldehydic H atoms and not an insertion into the CH bonds of the aldehyde nor other primary steps suggested recently in the literature.

INTRODUCTION

THE reaction of oxygen atoms with acetaldehyde was one of the first in a series of oxygen atom reactions studied in this Laboratory by one of the authors (R.J.C.). It was found[1] that the reaction with oxygen atoms produced by the mercury photosensitized decomposition of nitrous oxide yielded biacetyl and water as the main products. This indicated that the primary process involved the abstraction of the aldehydic H atom

$$CH_3CHO+O\rightarrow CH_3CO+OH, \qquad (1)$$

followed by

$$CH_3CHO+OH\rightarrow CH_3CO+H_2O, \qquad (2)$$

$$CH_3CO+CH_3CO\rightarrow CH_3CO\cdot COCH_3. \qquad (3)$$

The reaction of oxygen atoms with acetaldehyde was shown to be 0.7 ± 0.1 times as fast as the reaction of oxygen atoms with ethylene.

The only other investigation of this reaction has been made by Avramenko and his co-workers.[2–5] They

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† National Research Council Postdoctorate Fellow, 1963–1965.

[1] R. J. Cvetanović, Can. J. Chem. **34**, 775 (1956).

[2] L. I. Avramenko and R. V. Lorentso, Zh. Fiz. Khim. **26**, 1084 (1952).

[3] L. I. Avramenko, R. V. Kolesnikova, and M. F. Sorokina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk **1961**, 1005.

[4] L. I. Avramenko and R. V. Kolesnikova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk **1961**, 1231.

[5] L. I. Avramenko and R. V. Kolesnikova, Advan. Photochem. **2**, 25 (1964).

generated oxygen atoms by electrical discharge in molecular oxygen and alternatively in water vapor. In their initial investigation[2] at 100°C, they found a diversity of products and postulated the following primary steps:

$$CH_3CHO+O \rightarrow CO_2+CH_3+H, \qquad (4a)$$

$$\rightarrow CHO+HCHO+H, \qquad (4b)$$

$$\rightarrow CH_3COOH, \qquad (5)$$

with $k_4 > k_5 > k_1$. More recently[3] they have investigated the same reaction using an electrical discharge in molecular oxygen in a system where surface effects were reduced to a minimum. The products found were acetic acid and glycollic aldehyde at 100°C, and also water and ketene at room temperature. They suggested in addition to Reactions (4) and (5) the following other primary processes:

$$CH_3CHO+O \rightarrow OH\cdot CH_2CHO \qquad (6)$$

and, at room temperature,

$$CH_3CHO+O \rightarrow CH_2CO+H_2O. \qquad (7)$$

These conclusions are in direct contradiction with the earlier mentioned finding of Cvetanović that the primary step in the process is Reaction (1), i.e., a simple abstraction of the aldehydic H atom. For this reason Avramenko and Kolesnikova have also investigated[4] this reaction using the same technique as used by Cvetanović. They do not report any products for the reaction at low acetaldehyde pressures but at high acetaldehyde pressures report acetic acid as the only product. On the basis of these results, Avramenko and Kolesnikova have reiterated that there are several primary modes of attack by oxygen atoms including the scission of the CC bond, insertion of the oxygen atom into the aldehydic CH bond or into a CH bond of the methyl group, and the simultaneous abstraction of two hydrogen atoms, and that they are all more important than the abstraction of the aldehydic H atom.

The contradictory results obtained in these two independent studies have broader implications for the understanding of the general chemical behavior of oxygen atoms and similar reacting species. Thus, it has been recently shown[6] that the excited singlet oxygen atoms readily insert into the paraffinic CH bonds. The ground-state triplet oxygen atoms on the other hand do not insert although they do abstract the paraffinic hydrogen atoms. This difference in behavior of the two species is in agreement with the spin conservation rule since an insertion of the singlet atoms to give alcohol molecules in their ground electronic state does not require spin reversal while with the triplet atoms a spin reversal would be necessary. Similar differences in chemical behavior are exhibited also by the singlet and triplet methylene.[7] The conclusion of Avramenko and Kolesnikova that triplet oxygen atoms do insert into the CH bonds of acetaldehyde, while it cannot be ruled out *a priori*, is in disagreement with these findings. Since the experimental results of these authors also disagree with the earlier experimental results from this Laboratory, we have felt that the reaction must be carefully investigated once again. We have done this, using two different sources of oxygen atoms, and report the results in the present paper. The previously employed nitrous oxide technique was used again, and a careful analysis was made in particular for ketene and acetic acid, the compounds reported by Avramenko *et al.* to be the major reaction products. In addition, oxygen atoms were also generated by the photolysis of nitrogen dioxide at 3660 Å. As discussed by Sato and Cvetanović,[8] at this wavelength the ground-state oxygen atoms are initially formed in the photolytic reaction

$$NO_2+h\nu \rightarrow NO+O(^3P). \qquad (8)$$

They subsequently react rapidly with NO_2

$$O+NO_2 \rightarrow NO+O_2, \qquad (9)$$

but when acetaldehyde is added, it can compete efficiently with NO_2 for oxygen atoms.

EXPERIMENTAL

Acetaldehyde was a Matheson Company product and was thoroughly degassed and purified by bulb-to-bulb distillation *in vacuo*. It was degassed at −196°C before each run and distilled into a gas buret at −78°C. Nitrous oxide was obtained from British Oxygen Company, purified by bulb-to-bulb distillation *in vacuo* and degassed at −196°C before each run. Ketene was prepared by the pyrolysis of acetic anhydride *in vacuo* at 500°C[9] and was purified by bulb-to-bulb distillation. It was stored at liquid-nitrogen temperature and mass spectrometric analysis showed that no acetic anhydride was present. Hydrogen was a Linde Product and was not purified further. Nitrogen dioxide was obtained from Matheson Company and was purified by repeated bulb-to-bulb distillation *in vacuo* at −78°C. Nitric oxide was a Matheson Company product and was purified by passage through a molecular sieve 13X which had previously been outgassed at 350°C. Biacetyl

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[6] H. Yamazaki and R. J. Cvetanović, J. Chem. Phys. **41**, 3703 (1964).

[7] J. A. Bell, Progr. Phys. Org. Chem. **2**, 1 (1964).

[8] S. Sato and R. J. Cvetanović, Can. J. Chem. **36**, 970 (1958).

[9] G. F. Fisher, H. F. Maclean, and A. W. Schnizer, J. Org. Chem. **18**, 1055 (1953).

was an Eastman Organic Chemicals product and was purified by bulb-to-bulb distillation *in vacuo*.

The apparatus used in the experiments with nitrous oxide and acetaldehyde consisted of a cylindrical quartz vessel 5 cm in diameter and 10 cm long connected to an all-glass circulating pump supported on Teflon bearings. The circulating reaction system had a total volume of 403 ml. The products were fractionated and analyzed in the conventional type of analysis system described in detail previously.[10] The unreacted N_2O was pumped off from a Le Roy still at −150°C. Another fraction was recovered at −95°C; it contained unreacted acetaldehyde and some acetone. The room-temperature fraction contained acetone, biacetyl, water, and acetic acid.

The apparatus used in the experiments with nitrogen dioxide was mercury free. Stopcocks were lubricated with high-vacuum silicone grease (Dow Corning). Pressures were measured on a mercury-bellows gauge or a silicone oil manometer. The reaction cell was as described above except that it was made of Pyrex. It was connected to the vacuum line via a calibrated 6 ml volume in which small amounts of NO_2 could be measured and introduced into the reaction vessel intermittently during the photolysis. The cell was illuminated with a medium-pressure mercury arc (Hanovia *S* 500) through a set of two Corning glass filters (7–39 and 0–52) to give radiation at 3660 Å. The products were condensed in liquid nitrogen and any noncondensibles (NO and O_2) pumped off. The condensible products were transferred to a sampling tube and then to a mercury-containing high-vacuum apparatus. They were distilled to a trap containing a few drops of mercury which on warming removed the unreacted nitrogen dioxide. The products were recondensed in liquid nitrogen and the trap evacuated to remove nitric oxide.

The analysis of the products was carried out by gas–liquid chromatography, usually on a 12-ft dinonyl phthalate (20%) on Chromosorb W (H.M.D.S. treated) column at 83°C using helium as carrier gas. This column was not very efficient for the analysis of water, and better results were obtained using a polyethylene oxide (Pluronic P84 Wyandotte Chemical Corporation) on Chromosorb W (H.M.D.S. treated) column. Analysis for acetic acid was carried out by condensing the room-temperature fraction in 10 μl benzene, and on warming the sample was injected into a Perkin–Elmer Vapor Fractometer, Model 154. Acetic acid was separated from biacetyl and the solvent on a 12-ft trimer acid[11] (3%) on Teflon 6 column at 100°C using helium as carrier gas. A representative chromatogram is shown in Fig. 1. The identity of the major products separated by GLC was confirmed by infrared and mass spectrometric analysis.

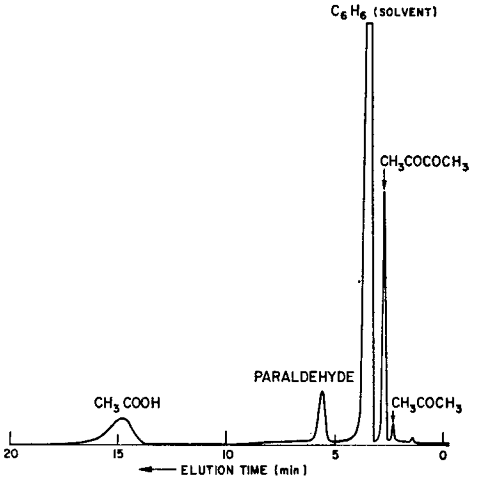

FIG. 1. Typical gas–liquid chromatogram for the analysis of acetic acid (column temperature 100°C).

RESULTS AND DISCUSSION

Nitrous Oxide Technique

It was shown previously[1] that this reaction can be studied only over a limited nitrous oxide to acetaldehyde ratio, and acetaldehyde pressure. At too low pressures of acetaldehyde large conversions of the reactant are unavoidable and result in secondary reactions of O atoms with the products. On the other hand, at a fixed pressure of 100-mm nitrous oxide, there is an excessive quenching of the Hg $6(^3P_1)$ atoms by acetaldehyde itself if its partial pressure is too high. Under such conditions the products of the mercury photosensitized decomposition are obtained, viz., CO, CH_4, C_2H_6, and H_2.

The results of a number of experiments carried out at different acetaldehyde pressures are given in Table I. The yield of products per oxygen atom consumed is shown in Fig. 2 as a function of acetaldehyde pressure. The products are biacetyl, water, and acetone. The yield of water has a constant value of unity over a pressure range where the primary attack of O atoms on acetaldehyde is assumed to predominate. The yield of biacetyl attains a maximum value of about 0.7 at an acetaldehyde pressure of 2 to 4 mm and then appears to decline slowly as the acetaldehyde pressure is increased, although the analytical scatter is appreciable. Acetone is a minor product and its yield increases with increasing acetaldehyde pressure.

In order to establish whether ketene and acetic acid are formed in the reaction, careful analysis was made for these two compounds. In a number of experiments, instead of pumping off the unreacted N_2O, only the C_2

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[10] R. J. Cvetanović, J. Chem. Phys. **23**, 1203 (1955).

[11] W. Averill, J. Gas. Chromatog. **1**, 22 (1963). F. J. Kabot and L. S. Ettre, *ibid.* p. 17.

TABLE I. Yield of the principal products per oxygen atom consumed in experiments with 100 mm N_2O and varying amounts of CH_3CHO. Photolysis time 20 min (25°C).

Run	CH_3CHO (mm)	N_2O (mm)	N_2 (μM)	Relative yields of products ($R_{N_2}=1$)						
				CO	CH_4	C_2H_6	H_2O	$(CH_3CO)_2$	CH_3COCH_3	$-\Delta CH_3CHO$
67	1.29	100.8	16.47	0.069	0.009	0.006	0.61	0.56	0.088	1.38
59	2.42	100.6	15.24	0.078	0.011	0.010	0.66	0.71	0.089	2.47
55	3.40	100.1	15.48	0.093	0.013	0.006	0.74	0.67	0.088	2.19
57	5.04	100.2	14.71	0.118	0.019	0.010	0.96	0.63	0.095	2.12
56	7.63	99.9	14.42	0.130	0.029	0.015	0.97	0.67	0.126	1.66
69	9.71	100.8	13.59	0.141	0.039	0.019		0.67	0.142	2.84
58	11.80	100.8	13.59	0.152	0.046	0.020	1.00	0.70	0.176	
63	14.39	100.2	11.58	0.179	0.054		1.02	0.51	0.166	

fraction was pumped off and the rest of the condensible products was trapped out. A small fraction of this sample was passed at a slow flow rate through a 300-ft dinonyl phthalate capillary column at 0°C. With a flame ionization detector, analysis of small traces of ketene was possible in the presence of large excess of N_2O. No ketene was detected. This result shows that ketene cannot be an important reaction product, although smaller amounts could have escaped detection in this manner.

In a series of experiments shown in Table II the room-temperature fraction was analyzed on the trimer acid column and the small yields of acetic acid were determined. The maximum yield per O atom consumed is 0.007. Even at long exposure times (120 min), acetic acid is still a very minor product. Hence any reaction responsible for the formation of acetic acid, whether primary or secondary, is of little importance.

One possible source of acetic acid is from the reaction of small amounts of ketene, which are likely to be present, with the water formed in the reaction. To test this, a series of experiments were carried out in which traces of ketene were added to the reactants. The results, given in Table III, show that the acetic acid yield does increase.

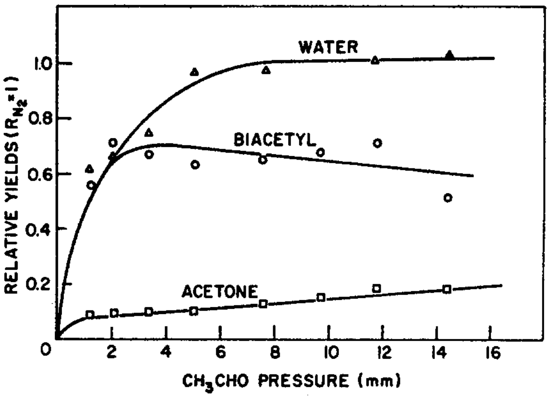

FIG. 2. Yields of products per oxygen atom consumed at 100 mm of N_2O and varying pressures of acetaldehyde. Exposure time 15 min.

The results of these experiments are fully consistent with the mechanism postulated previously by Cvetanović,

$$CH_3CHO+O\rightarrow CH_3CO+OH, \qquad (1)$$

$$CH_3CHO+OH\rightarrow CH_3CO+H_2O, \qquad (2)$$

$$CH_3CO+CH_3CO\rightarrow CH_3CO\cdot COCH_3. \qquad (3)$$

The yield of biacetyl per oxygen atom lower than unity indicates that acetyl radicals are being consumed also in other reactions. As the acetaldehyde pressure increases so does the amount of direct quenching by acetaldehyde resulting in the formation of CH_3 and HCO radicals. Hence acetone results from the radical combination reaction

$$CH_3CO+CH_3\rightarrow CH_3COCH_3. \qquad (10)$$

Other reactions which are likely to consume acetyl radicals are

$$CH_3CO+CH_3\rightarrow CH_4+CH_2CO, \qquad (11)$$

$$CH_3CO+CH_3CO\rightarrow CH_3CHO+CH_2CO, \qquad (12)$$

$$CH_3CO+HCO\rightarrow CH_3CHO+CO. \qquad (13)$$

Although Reactions (11) and (12) play a minor role in the process, the small amount of ketene formed is probably responsible for the formation of the traces of acetic acid by the reaction

$$CH_2CO+H_2O\rightarrow CH_3COOH. \qquad (14)$$

Photolysis of Nitrogen Dioxide

Further experiments were carried out using the photolysis of NO_2 at 3660 Å as the source of O atoms. At this wavelength acetaldehyde is not photolyzed and there are therefore no complications from its decomposition. No evidence for any dark reaction was found at room temperature, in agreement with previous

TABLE II. Yield of acetic acid and biacetyl in experiments with 100 mm N_2O and varying amounts of CH_3CHO (25°C).

Run	CH_3CHO (mm)	N_2O (mm)	Photolysis time (min)	N_2 (μM)	CH_3COOH (μM)	Biacetyl (μM)	Yield relative to N_2: CH_3COOH	Yield relative to N_2: Biacetyl	Yield relative to N_2: CH_3COOH/biacetyl
60	7.96	100.0	20	16.84	0.065	10.1	0.0039	0.60	0.006
61	12.15	100.2	20	13.74	0.073	9.3	0.0068	0.68	0.010
62	21.57	100.6	20	12.18	0.042	7.0	0.0057	0.58	0.010
36	2.24	100.0	120	73.4	0.15	8.8	0.0020	0.12	0.016
37	4.35	100.0	120	79.7	0.27	23.9	0.0034	0.30	0.011
31	5.34	100.2	120	89.7	0.38	36.8	0.0042	0.41	0.010
34	8.12	100.3	120	90.8	0.90	56.4	0.0100	0.62	0.016
35	10.91	100.2	120	77.5	1.00	50.4	0.0129	0.65	0.020

investigations of the thermal reaction between acetaldehyde and NO_2.[12–14]

It has been shown[15] that $k_9/k_1 \sim 18$, so that NO_2 reacts much more rapidly than acetaldehyde with O atoms. In order to suppress Reaction (9), a large excess of acetaldehyde over NO_2 was used. By adding small amounts of NO_2 intermittently during the reaction the ratio $(NO_2)/(CH_3CHO)$ never exceeded 0.015.

The major product of the reaction was carbon dioxide, together with methyl nitrate, nitromethane, and methyl nitrite. The results of a series of experiments at a constant ratio of reactants carried out at different irradiation times are shown in Table IV and are plotted in Fig. 3. Acetic acid was not found among the products of the reaction, although when added to the reactants in trace amounts, it was recovered after the photolysis. Acetic acid is therefore not a primary product in the reaction of oxygen atoms with acetaldehyde. Ketene was found to react rapidly on mixing with NO_2 so that this series of experiments cannot give any information regarding its role in the process (although the nitrous oxide experiments showed it to be unimportant, as discussed above).

An unsuccessful attempt was made to detect CH_3CONO_2, but this compound is probably unstable and will dissociate readily. The products actually observed are consistent with the following mechanism in which acetyl radicals are formed in the primary reaction and then react further with NO_2:

$$CH_3CHO+O \rightarrow CH_3CO+OH, \tag{1}$$

$$CH_3CHO+OH \rightarrow CH_3CO+H_2O, \tag{2}$$

$$CH_3CO+NO_2 \rightarrow CH_3CO_2+NO, \tag{15}$$

$$CH_3CO_2 \rightarrow CH_3+CO_2, \tag{16}$$

$$CH_3+NO_2 \rightarrow CH_3NO_2, \tag{17}$$

$$CH_3+NO_2 \rightarrow CH_3O+NO, \tag{18}$$

$$CH_3O+NO_2 \rightarrow CH_3ONO_2, \tag{19}$$

$$CH_3O+NO \rightarrow CH_3ONO. \tag{20}$$

Water was not detected as a reaction product and it is assumed to be removed by reaction with NO_2.

In the presence of added NO (Run 24, Table IV), it is seen that Reactions (17), (18), and (19) tend to be suppressed, while Reaction (15) is affected little. No attempt was made to analyze for CH_3NO.

The above scheme is in agreement with the results of other workers who have investigated systems in which acetyl radicals are formed in the presence of

TABLE III. Effect of traces of ketene on the yield of acetic acid in CH_3CHO–N_2O experiments (25°C).

Run	CH_3CHO (mm)	CH_2CO (μM)	N_2O (mm)	CH_2CO/CH_3CHO	Photolysis time (min)	N_2 (μM)	CH_3COOH (μM)	$\frac{CH_3COOH}{N_2}$
60	7.96	0	100.0	0	20	16.84	0.065	0.004
66	7.66	2.04	100.3	0.012	20	14.64	0.055	0.004
65	7.61	5.10	100.3	0.031	20	13.89	0.10	0.007
64	7.49	10.9	100.3	0.067	20	7.18	0.17	0.024

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[12] C. A. McDowell and J. H. Thomas, Trans. Faraday Soc. **46**, 1030 (1950).

[13] L. C. Browning (private communication).

[14] A. E. Pedler and F. H. Pollard, Trans. Faraday Soc. **53**, 44 (1957).

[15] R. J. Cvetanović, Advan. Photochem. **1**, 115 (1963).

TABLE IV. Yield of products in experiments in CH_3CHO–NO_2 mixtures at 3660 Å (25°C).

Run	CH_3CHO (mm)	NO_2[a] (mm)	NO (mm)	Photolysis time (min)	CO_2 (μM)	CH_3ONO_2 (μM)	CH_3NO_2 (μM)	CH_3ONO (μM)
23	9.9	1.45		15	3.16	0.88	0.73	0.44
22	10.0	1.45		30	4.50	1.03	1.40	0.81
20	10.0	1.45		45	6.39	1.01	1.99	1.11
19	9.9	1.45		60	7.51	0.97	2.18	1.36
18	10.0	1.45		90	8.86	0.99	2.44	1.77
21	10.0	1.45		120	8.64	0.89	2.58	2.03
24	10.0	1.45	1.54	30	4.05	0.13	0	0.90

[a] The total amounts of NO_2 introduced are represented by 1.45 mm. This has been divided into 10 intermittent doses, as explained in the text.

NO_2. Browning[13] studied the thermal reaction of acetaldehyde with NO_2 in the temperature range 100°–130°C and found the same products as observed in present work. Pedler and Pollard[14] investigated the same reaction at temperatures above 100°C and found carbon dioxide and nitric oxide as the main gaseous products. Phillips and Shaw[16] in their recent investigation of the reaction of methyl and methoxy radicals with NO_2 and NO used acetaldehyde as their source of methyl radicals, and obtained identical products. In all the above investigations, acetyl radicals were assumed to be formed by the thermal bimolecular reaction

$$CH_3CHO+NO_2 \rightarrow CH_3CO+HNO_2. \qquad (21)$$

At room temperature and with the ratio of reactants used in the present experiments, Reaction (21) will not be important.

Photolysis of Biacetyl–NO_2 Mixtures at 2537 Å

In order to gain further information on the behavior of acetyl radicals in the presence of NO_2, the photolysis of biacetyl–NO_2 mixtures was studied at 2537 Å. The results are shown in Table V. At this wavelength biacetyl absorbs strongly whereas the extinction coefficient of NO_2 is at a minimum so that photolysis of NO_2, Reaction (8), is unimportant. The direct photolysis of biacetyl yields acetyl radicals[17] which then react with NO_2 and, as evident from the data in Table V, form carbon dioxide, methyl nitrate, and nitromethane. No analysis for methyl nitrite was attempted in this series. It should be noted that CO_2 is not a product of the photolysis of biacetyl alone (Runs 11 and 12) but is formed readily in the presence of NO_2 (Runs 8, 7, and 10).

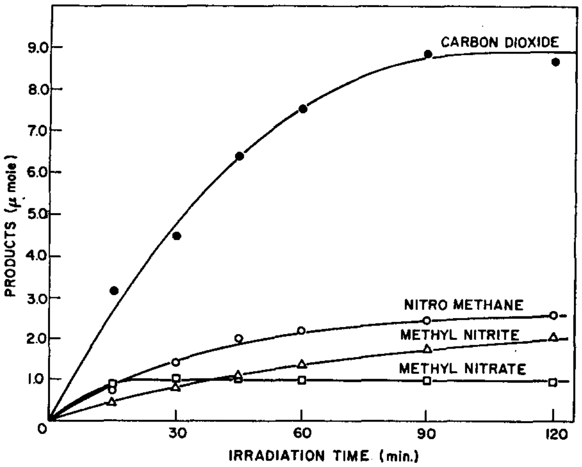

FIG. 3. Yields of products as a function of irradiation time in acetaldehyde–NO_2 mixtures.

The photolyses of biacetyl–NO_2 mixtures at 2537 Å and of acetaldehyde–NO_2 mixtures at 3660 Å provide therefore further evidence for the postulate that the primary attack of the ground-state oxygen atoms on CH_3CHO results in the abstraction of the aldehydic H atom. They also demonstrate that the ground-state oxygen atoms do not insert to form acetic acid as a primary product.

CONCLUSIONS

The results of the present experiments confirm the earlier finding by Cvetanović[1] that the ground-state oxygen atoms react with acetaldehyde in a simple manner and that is by abstracting the aldehydic H atom. There is no evidence for any other *primary* reactions of the ground-state oxygen atoms, such as their ability to induce scission of the CC bond or to insert into the CH bonds, as postulated by Avramenko *et al.* In view of these findings, it is necessary to discuss the possible reasons for the discrepancy between the results obtained from the studies in this Laboratory and those by Avramenko *et al.* The latter authors have used the electrical discharge techniques and flow systems. Apart from such potential complicating factors as the presence of appreciable concentrations of reactive species (O_2, H, OH) other than those primarily studied (O), which can be eliminated to a smaller or greater extent, there is one feature of such

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[16] L. Phillips and R. Shaw, Symp. Combust., 10th, Cambridge University, 1964, 453 (1965).

[17] F. E. Blacet and W. E. Bell, Discussions Faraday Soc. **14**, 70 (1953).

TABLE V. Yield of products in experiments in biacetyl—NO_2 mixtures at 2537 Å (25°C).

Run	Biacetyl (mm)	NO_2 (mm)	Photolysis time (min)	CO (μM)	CH_4 (μM)	C_2H_6 (μM)	CO_2 (μM)	CH_3ONO_2 (μM)	CH_3NO_2 (μM)
8	10.1	1.35	5	2.99	0	0	2.38	1.07	0.80
7	10.0	1.35	15	8.40	0.09	0	4.26	1.31	1.60
10	10.1	1.35	30	18.5	0.43	0.50	5.55	···	···
11	10.1	0	15	18.6	0.40	4.50	0	0	0
12	9.9	0	60	49.4	1.00	13.8	0	0	0

techniques which, as will be shown below, must lead to complications under the usually employed conditions and which must be recognized. In the flow systems of this type the concentration of the atomic species studied (O atoms) must be relatively high so that sufficient concentration of products may be obtained to permit analysis. Thus, in studying the present reaction, the ratio $(CH_3CHO)/(O)$ will normally be very much smaller than is necessary to suppress the very fast occurring atom–radical reactions. This can be readily shown by considering the following reactions:

$$CH_3CHO+O\rightarrow CH_3CO+OH, \qquad (1)$$

$$CH_3CHO+OH\rightarrow CH_3CO+H_2O, \qquad (2)$$

$$CH_3CO+CH_3CO\rightarrow CH_3CO\cdot COCH_3, \qquad (3)$$

$$CH_3CO+O\rightarrow \text{products}, \qquad (22)$$

$$CH_3CO+OH\rightarrow \text{products}. \qquad (23)$$

Assuming that Reactions (3), (22), and (23) occur at each collision and applying a steady-state treatment to the acetyl radical concentration we obtain for the ratio of the rates of Reactions (22) and (1)

$$\frac{R_{22}}{R_1}=\frac{k_{22}}{k_1}\frac{(O)}{(CH_3CHO)}\left\{\left(1+\frac{16k_1}{k_{22}}\frac{(CH_3CHO)}{(O)}\right)^{\frac{1}{2}}-1\right\}.$$

Assuming k_{22} is equal to the collision frequency, the ratio k_1/k_{22} will be close to 10^{-4}. Substitution in the above equation shows that even at a ratio of

$$(CH_3CHO)/(O)=100, \ R_{22}/R_1=1.9,$$

but at

$$(CH_3CHO)/(O)=10^8, \ R_{22}/R_1=0.01.$$

Hence unless the concentration of O atoms relative to CH_3CHO is very small, products will be obtained from Reactions (22) and (23). As already mentioned, when the electrical discharge technique is applied to flow systems, the ratio of the atomic species to that of the reactant cannot, as a rule, be kept low for analytical reasons. It is therefore possible that in the experiments of Avramenko *et al.* acetic acid resulted from Reaction (23) [or from Reaction (22) followed by H abstraction] and ketene from Reaction (22).

It is more difficult to explain the conflicting results obtained by Avramenko and Kolesnikova using the nitrous oxide technique. They obtained only acetic acid as their product, and then only at a $(N_2O)/(CH_3CHO)$ ratio of 2 and total gas pressure of 432 mm. It should be pointed out that under these conditions the mercury photosensitized decomposition of acetaldehyde predominates. Also, at such high pressures of acetaldehyde it may be difficult to avoid the presence of a trace of acetic acid as an impurity in acetaldehyde. Avramenko and Kolesnikova used chemical tests for their analysis. Their failure to observe any products at a total gas pressure of 50 mm and using a similar ratio of reactants as in experiments listed in Tables I and II suggests low analytical sensitivity. The suggested explanation that at low acetaldehyde pressures nitrous oxide competes with acetaldehyde for oxygen atoms is untenable because ground-state oxygen atoms react with nitrous oxide extremely slowly.[18]

Avramenko and Kolesnikova suggest that their failure to find biacetyl shows that either acetyl radicals are not formed, or if formed, they do not recombine into biacetyl but only disproportionate as in Reaction (12). Thus for their experiments with acetaldehyde and H atoms, they suggest that the primary step is an abstraction of the aldehydic H atom to give acetyl radicals

$$CH_3CHO+H\rightarrow CH_3CO+H_2, \qquad (24)$$

but that the acetyl radicals give ketene rather than biacetyl. In contrast to this, in an experiment carried out in this Laboratory using the same technique, mercury photosensitization of 5 mm of acetaldehyde and 50 mm of hydrogen yielded biacetyl as the main product. Similar results were also obtained at the Union Carbide Corporation by Meisels[19] who found biacetyl as the main product of the hydrogen sensitized radiolysis of acetaldehyde. Since in a reaction of hydrogen atoms with acetaldehyde Avramenko and Kolesnikova again did not detect any biacetyl, it appears very likely that the conflicting results in the oxygen atom–acetaldehyde reaction using the nitrous oxide technique may be due to the limited sensitivity of the analytical technique used by these workers.

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[18] F. C. Henriques, Jr., A. B. F. Duncan, and W. A. Noyes, Jr., J. Chem. Phys. 6, 518 (1938).

[19] G. G. Meisels (private communication).