TABLE V

POSSIBLE RADICAL–RADICAL RECOMBINATION REACTIONS

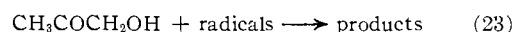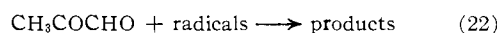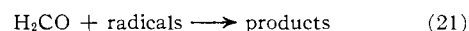| R_1	CH₃	CH₃O	CH₃CO	CH₃COO	HCO	HCOO	CH₃COCH₂	CH₃COCH₂O	HO
CH₃	X	?	?	?	?	?	?	X	O
CH₃O		O	?	X	?	X	X	X	O
CH₃CO			X	X	?	X	X	X	O
CH₃COO				X	X	X	X	X	X
HCO					X	?	X	X	O
HCOO						X	X	X	O
CH₃COCH₂							X	X	O
CH₃COCH₂O								X	X
HO									X

disproportionation reactions, two direct oxygen–radical reactions, and the heterogeneous decomposition of CH₃OOH. Water could be formed by 20 different radical–radical reactions involving HO, plus the heterogeneous decomposition of CH₃OOH, and possibly heterogeneous destruction of HO₂. Methanol could be formed in 13 different radical–radical reactions. Methyl hydroperoxide is possible from 13 such reactions. There appears, however, to be only one source of CH₃OOCH₃, and its rate of formation is a qualitative measure of the CH₃O radical concentration.

Undoubtedly these 140 possibilities could be reduced by other arguments, based on energetics, the literature, and aesthetics. However, products were observed at only 12 mass peaks; the initial rates plus curves of growth give at most 24 data. It appears clear that in spite of the great detail in which the products are followed, this investigation is not sufficient to give the first approximation to a definitive mechanism. Furthermore, the analysis of all molecular products is insufficient to establish the mechanism.

On the other hand, this investigation does give some mechanistic conclusions. The low yield of CH₃OOCH₃ and the high yield of CH₃OOH indicates some very easily abstracted hydrogen and an unusually abundant source of free radicals formed either by (i) oxygen molecule attack on excited acetone molecules or (ii) oxygen attack on the acetyl radical.

Subsequent Reactions.—As the reaction proceeds the products enter the reaction. For example, the

half-life data clearly indicate that H₂CO, CH₃COCHO, CH₃COCH₂OH, and CH₃OOH are removed. Since the first three products are stable in the dark, their removal must be due to free radical attack

$$H_2CO + \text{radicals} \longrightarrow \text{products} \qquad (21)$$

$$CH_3COCHO + \text{radicals} \longrightarrow \text{products} \qquad (22)$$

$$CH_3COCH_2OH + \text{radicals} \longrightarrow \text{products} \qquad (23)$$

where the products probably include H₂O, CO, and CO₂. The methyl hydroperoxide decays both in the dark and when illuminated, the decay when illuminated being somewhat greater than in the dark under the same conditions. Thus, the reactions indicated are[10]

$$CH_3OOH \xrightarrow{\text{wall}} H_2CO + H_2O \qquad (24)$$

$$CH_3OOH + \text{radicals} \longrightarrow \text{products} \qquad (25)$$
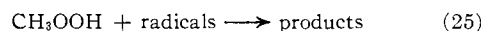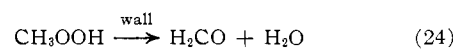
Apparently, reaction 21 is more important than reaction 24, and the net effect is a diminution of the relative H₂CO pressure with time. The products of reactions 21–23 presumably include H₂O, CO, and CO₂, and thus these products should be examples of case 4 of article I. Analysis of the data does show that all of these products are greater at the steady state than would be predicted solely from the initial reactions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Photochemical Oxidations. IV. Acetaldehyde

BY HAROLD S. JOHNSTON AND JULIAN HEICKLEN

The room-temperature photooxidation of acetaldehyde (0.4 to 18 mm.) in oxygen (1.0 to 9.2 mm.) with continuous ultraviolet radiation above 2200 Å. has been studied by the method outlined in part I of this series. Observations were made by leaking the reaction mixture directly into the electron beam of the mass spectrometer during photolysis. The principal products of reaction were CH₃OH and presumably CO and CO₂; other products were H₂O, CH₂O, HCOOH, CH₃OOH, CH₃COOH, CH₃OOCH₃, and probably CH₃C(O)OOH. Because of the cracking pattern of the reactants, it was impossible to establish the presence or absence of CH₄, CH₂CO, CO, and CO₂. Oxidation of the primary radicals, CH₃ and HCO, leads to CH₃OO, CH₃O, HO, and HO₂, and probably HCO(OO) and HCOO. There are at least six radicals in this system that can disproportionate in 36 ways and undergo other reactions. Thus this reaction is much too complicated for its mechanism to be revealed merely by analysis of all products.

Introduction

The room-temperature photooxidation of acetaldehyde in the vapor phase, in liquid, and in solution was first studied by Bowen and Tietz.[1] They found the

product(s) of reaction to be a peroxide(s) formed in a chain length of about 1000. Presumably, the peroxide(s) was peracetic acid and/or diacetyl peroxide.

(1) E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930).

TABLE I

INITIAL RATES OF PRODUCT FORMATION

	1	2	3	4ᵃ	5	6	7	8	9	10
					Series					
$[O_2]$, mm.	1.5	9.2	1.0	1	1.0	8.9	0.90	0.9	1.3	1.3
$[CH_3CHO]$, mm.	0.45	0.40	1.5	2	4.0	7.3	7.0	7.0	18	18
λ_{min}, Å.	2200	2200	2200	2200	2200	2200	2200	2800	2200	2200
Neutral density screens	None	None	None	None	None	None	None	None	None	8.8%
$R^0 \times 10^3/[CH_3CHO]$, μ of prod./mm. of CH_3CHO-sec.										
H_2O (obsd.)	575	16.5	58 (80)ᵇ	...	...	30	32	11.8	...	...
CH_2O (obsd.)	162	...	19.6	...	...	14.3	17.0	5.9 / 3.8	...	...
(calcd.)ᶜ	172	...	17.2	(~4)	(~13)	14.3	17.3	5.0	(~13)	...
CH_3OH (obsd.)	191	6.0	60	...	...	85	97	24	...	...
(calcd.)	226	5.6	63	(64)	(57)	60	103	27	(76)	(5.9)
HCOOH (obsd.)	4.5	...	1.4	...	...	3.5	2.7	0.7	...	...
(calcd.)	4.2	(0.32)	(1.3)	(3)	(>2.3)	3.5	2.6	(0.61)	(2.3)	..
CH_3OOH (obsd.)	114	18.5	18.2	...	...	19.8	12.5	3.3	...	...
(calcd.)	110	19.5	18.7	(13.9)	(9.8)	18.1	13.3	3.3	(6.8)	...
CH_3COOH (obsd.)	20.4	1.0	3.5	...	...	4.8	4.2	2.2	...	...
(calcd.)	21.0	1.03	4.0	(4.2)	(4.2)	5.4	4.9	2.4	(4.4)	(1.7)
$CH_3C(O)OOH$ (obsd.)	0.46	...	0.14	...	...	0.30	0.27	0.082	...	...
(calcd.)	0.34	...	0.12	(0.34)	(0.14)	0.29	0.29	0.099	(0.44)	(0.11)
$(CH_3O)_2$ (obsd.)	7.3	...	1.5	...	...	2.2	1.46	0.41	...	...
(calcd.)	6.6	...	1.3	(1.4)	(1.1)	(1.2)ᵈ	1.5	0.47	(1.2)	(0.07)

ᵃ Series 4, 5, 9, and 10 done with different gold foil.   ᵇ Numbers in parentheses are uncertain.   ᶜ R_x^0(calcd.) = 0.69 P_x^{ss}/τ_L.   ᵈ Used τ_L of 200 sec.

Carruthers and Norrish[2] photooxidized formaldehyde and acetaldehyde. Except for the length of the chain, their results with acetaldehyde were consistent with those of Bowen and Tietz. They also found the photooxidation of formaldehyde to proceed *via* a short chain at 100°, but neither the performic acid nor diformyl peroxide was observed. The products were HCOOH and H_2, CO_2, CO, and H_2O which were believed to come from the formic acid. In 1941, Mignolet[3] photooxidized acetaldehyde and obtained results in agreement with those of ref. 1 and 2. More recently, McDowell and his co-workers[4-6] have confirmed the presence of peracetic acid as a product in the photooxidation of acetaldehyde. Calvert and Hanst[7] studied the photooxidation at lower pressures (42 mm. of CH_3CHO) and found CO_2, CH_3OH, HCOOH, and CO as well as CH_3COOH and $CH_3C(O)OOH$. The surprising feature is that little or no CH_2O was found. In these experiments, peracetic acid was still the major product of reaction.

In keeping with the program of photochemical oxidations undertaken by us,[8] the acetaldehyde-oxygen system was studied at total pressures of less than 20 mm. to suppress even further the formation of peracetic and acetic acids. In this way it was hoped to obtain information concerning the oxidation of CH_3 and HCO radicals.

Experimental

The apparatus and experimental procedures have been described fully in the preceding articles of this series.[8]

(2) J. E. Carruthers and R. G. W. Norrish, *J. Chem. Soc.*, 1036 (1936).

(3) J. Mignolet, *Bull. soc. roy. sci. Liege*, 343 (1941).

(4) C. A. McDowell and J. B. Farmer, "Fifth (International) Symposium on Combustion," Reinhold Publishing Corp., New York, N. Y., 1955, p. 453.

(5) C. A. McDowell and L. K. Sharples, *Can. J. Chem.*, **36**, 251 (1958).

(6) C. A. McDowell and S. Sifniades, *ibid.*, **41**, 300 (1963).

(7) J. G. Calvert and P. L. Hanst, *ibid.*, **37**, 1671 (1959).

(8) J. P. Heicklen and H. S. Johnston, *J. Am. Chem. Soc.*, **84**, 4030, 4394 (1962).

Ten series of runs were made with variation of the oxygen and acetaldehyde pressures, the incident intensity, and the incident radiation. All series except series 8 were made with a Corning 9-54 filter, which eliminates all radiation below 2200 Å. In series 8, a Corning 0-53 filter was used to eliminate radiation below 2800 Å. Replications of series 1 through 3 and 6 through 8 were made; agreement was to within 10 to 15% except in a few scattered cases. In series 4, 5, 9, and 10, initial rates were not measured, and only the steady-state concentrations were measured. Matheson tank oxygen was used, and impurities were 0.3% argon and 0.7% nitrogen. Mallinckrodt acetaldehyde was used. A number of minor impurity peaks are present in its mass spectrum. Except in the case of diethyl ether, which is present at an impurity level of about 0.1%, the impurity peaks are all less than 0.01%.

Results

During irradiation, product peaks were observed at m/e = 17, 18, 30, 31, 46, 47, 48, 60, 61, and 62. The first eight peaks are readily identified with H_2O (17 and 18), CH_2O (30), CH_3OH (31), HCOOH (46), CH_3OOH (47 and 48, also part of 30 and 31), and CH_3COOH (60). The 62 peak corresponds to CH_3-$OOCH_3$. The small peak at m/e = 61 is not so easy to identify but probably corresponds to a major cracking peak of $CH_3C(O)OOH$; because it is an odd number, it cannot be a parent peak. The absolute pressures of the products were estimated from calibrations, comparison with the literature, and interpolation among related compounds. However, it is reemphasized that some of the calibration values may be in error by as much as 30 or 40%.

It was observed also that very minor product peaks occurred at m/e = 73, 77, 87, and 92, whereas the impurity peak at m/e = 72 diminished during irradiation. Presumably, impurity is attacked giving rise to additional products. However, these are very minor, are not connected with the primary oxidation, and consequently will be ignored.

Because of background cracking peaks, analyses could not be made for CO_2 (44), CH_2CO (42), CO

TABLE II
STEADY-STATE PRESSURES OF PRODUCTS

	\-Series-									
	1	2	3	4	5	6	7	8	9	10
$[O_2]$, mm.	1.5	9.2	1.0	1	1.0	8.9	0.90	0.9	1.3	1.3
$[CH_3CHO]$, mm.	0.45	0.40	1.5	2	4.0	7.3	7.0	7.0	18	18
λ_{min}, Å.	2200	2200	2200	2200	2200	2200	2200	2800	2200	2200
Neutral density screens	None	None	None	None	None	None	None	None	None	8.8%
$P^{ss}/[CH_3CHO]$, μ of prod./mm. of CH_4CHO										
H_2O	131	14.6	20.3	21.8	...	10.2	11.8	3.8	5.0	...
CH_2O	41	...	5.2	(~1)	(~3.3)	3.5	4.0	1.31	(~3.4)	...
CH_3OH	59	1.7	23	18.4	16.6	16	29	6.4	22	~1.7
$HCOOH$	1.2	0.09	0.36	0.8	>0.7	0.75	0.66	0.18	0.7	...
CH_3OOH	13.5	2.4	3.5	2.6	1.85	3.4	2.6	0.77	1.27	...
CH_3COOH	5.0	0.30	1.67	1.25	1.25	1.36	1.85	0.86	1.25	0.50
$CH_3CO(OOH)$	0.10	...	0.044	0.10	0.042	0.069	0.089	0.030	0.13	0.031
$(CH_4O)_2$	1.92	...	0.47	0.4	0.32	0.35	0.39	0.115	0.34	0.020
$m/e = 72$	...	...	...	0	-0.19	...	...	...	-0.19	...
$m/e = 73$	...	...	...	0	0.04	...	...	...	0	...
$m/e = 77$	...	...	...	0	0	...	...	...	0.13	0.035
$m/e = 87$	...	...	...	0	0	...	...	...	0.05	0.02
$m/e = 92$	...	...	...	0	0	...	...	...	0.02	...

TABLE III
HALF-LIVES OF PRODUCTS

	\-Series-								
	1	2	3	4	5	6	7	8	
$[O_2]$, mm.	1.5	9.2	1.0	1	1.0	8.9	0.90	0.9	
$[CH_3CHO]$, mm.	0.45	0.40	1.5	2	4.0	7.3	7.0	7.0	
λ_{min}, Å.	2200	2200	2200	2200	2200	2200	2200	2800	
Neutral density screens	None	None	None	None	None	None	None	None	
τ_D, sec.									Average
H_2O	290 ± 20	215 ± 30	340 ± 50	...	...	250 ± 20	235 ± 10	330 ± 50	275 ± 43
CH_2O	220 ± 20	...	210 ± 20	...	...	170 ± 20	160 ± 10	270 ± 40	210 ± 32
CH_3OH	210 ± 10	220 ± 40	195 ± 10	...	...	180 ± 10	175 ± 5	...	200 ± 16
$HCOOH$	250 ± 50	...	175 ± 40	...	...	190 ± 20	180 ± 10	...	200 ± 26
CH_3OOH	135 ± 10	115 ± 20	170 ± 20	...	..	140 ± 10	160 ± 10	150 ± 10	145 ± 15
CH_3COOH	270 ± 20	320 ± 60	265 ± 20	..	..	185 ± 10	160 ± 10	210 ± 10	235 ± 50
$CH_3C(O)OOH$	280 ± 50	..	250 ± 30	..	...	170 ± 10	180 ± 10	205 ± 20	215 ± 38
$(CH_4O)_2$	170 ± 40	...	180 ± 40	...	...	250 ± 20	165 ± 10	170 ± 20	190 ± 27
								Average	210 ± 31
τ_L, sec.									Average
H_2O	195 ± 20	1200 ± 100	390 ± 40	...	...	285 ± 20	550 ± 30	400 ± 20	500 ± 240
CH_2O	165 ± 20	...	210 ± 10	...	...	170 ± 10	160 ± 5	180 ± 30	180 ± 15
CH_3OH	180 ± 10	210 ± 30	250 ± 25	...	...	185 ± 15	195 ± 5	165 ± 20	200 ± 23
$HCOOH$	200 ± 100	...	...	...	...	150 ± 30	180 ± 10	...	185 ± 18
CH_3OOH	85 ± 5	85 ± 5	130 ± 10	...	...	130 ± 10	135 ± 10	160 ± 20	120 ± 24
CH_3COOH	165 ± 10	200 ± 50	285 ± 20	...	...	172 ± 5	260 ± 10	250 ± 20	220 ± 43
$CH_3C(O)OOH$	200 ± 100	...	250 ± 40	...	...	165 ± 10	210 ± 10	210 ± 20	210 ± 20
$(CH_3O)_2$	200 ± 30	...	250 ± 40	...	...	105 ± 5	165 ± 15	170 ± 20	180 ± 38
								Average	224 ± 52

(28), and CH_4 (16). Carbon dioxide and carbon monoxide are surely present.[7]

The experimental results are listed in Tables I through III. For all of the products, there are listed the initial rates, R_i; the steady-state partial pressure, P^{ss}; the half-time build-up to the steady-state pressure, τ_L; and the half-time of decay from the steady-state value after the light was turned off, τ_D. In Table I, the observed rates are those from the initial slopes of the curves of growth of the products. The calculated initial rates are found from the relationship

$$R_i(\text{calcd.}) = 0.69 P^{ss}/\tau_L \qquad (1)$$

as described in part I of this series. The steady state is reached when the rate for formation of the product equals its rate of removal, both by chemical processes and by effusion through the pinhole into the mass spectrometer.

If the only unobserved products are CO and CO_2, their sum can be estimated from the carbon–hydrogen mass balance

$$R_i(\text{CO}) + R_i(\text{CO}_2) = 0.5 R_i(\Sigma H) - R_i(\Sigma C) \qquad (2)$$

where $R_i(\Sigma H)$ is the sum of the initial rates of hydrogen atom production in the products and $R_i(\Sigma C)$ is the corresponding quantity for carbon atoms. These quantities are listed as entries 3 through 5 in Table IV for series 1 through 3 and 6 through 8. It is readily apparent that CO and CO_2, along with CH_3OH, are the major products of the reaction.

The results can be summarized in phenomenological terms, from the classification of part I, with no reference to the mechanism. (1) The observed initial products are H_2O, CH_2O, CH_3OH, $HCOOH$, CH_3OOH, CH_3COOH, CH_3OOCH_3, and probably $CH_3C(O)OOH$. (2) Water, the major product at low CH_3CHO pressures,

TABLE IV

ANALYSIS OF DATA

		Series					
Entry		1	2	3	6	7	8
1	$[O_2]$, mm.	1.5	9.2	1.0	8.9	0.90	0.9
2	$[CH_3CHO]$, mm.	0.45	0.40	1.5	7.3	7.0	7.0
3	$R_i(\Sigma H)/2[CH_3CHO]$	1291	68	233	265	276	74
4	$R_i(\Sigma C)/[CH_3CHO]$	519	29	108	134	135	39
5	$\{R_i(CO) + R_i(CO_2)\}/[CH_3CHO]$	772	39	125	131	141	35
6	$R_i(CH_2O)/R_i(CH_3OOCH_3)$	22		13	6.5 (12)	12	12

decreases in importance as the CH_3CHO pressure is raised. (3) CH_2O is always in smaller amounts than is CH_3OH. At the low pressure of CH_3CHO (0.4 mm.), the rates of production of these two products are similar, but at higher pressures the ratio $R_i(CH_2O)/R_i(CH_3OH)$ is about 0.2. (4) The rate of CH_3OOH formation relative to CH_3OH is markedly enhanced as the oxygen pressure is raised. (5) $HCOOH$, CH_3COOH, $CH_3C(O)OOH$, and CH_3OOCH_3 are minor products. (6) The half-lives of products in Table III give diagnostic information about products in the system as discussed in terms of curves of growth in part I of this series. The half-life for emptying the reaction cell by diffusion through the pinhole is about 210 sec. In the dark CH_3OOH disappears much faster and H_2O disappears much slower. This behavior indicates heterogeneous destruction of CH_3OOH to form H_2O as a product. The other product is presumably CH_2O, but its half-life in the cell is normal. Thus formaldehyde from CH_3OOH presumably remains as a polymer on the surface. In the illuminated cell the same pattern applies: water appears slowly (that is, it is formed by secondary processes as well as initial processes) and methyl hydroperoxide appears rapidly (it undergoes secondary destruction). Formaldehyde seems to have a short half-life in the light and also CH_3OOCH_3 and $HCOOH$, but these effects are not large or certain.

Discussion

The first problem is that of the primary photochemical products. Apparently acetaldehyde decomposes both by a molecular and a free radical split.[9]

$$CH_3CHO + h\nu \longrightarrow CH_4 + CO \qquad (3)$$

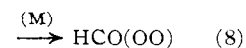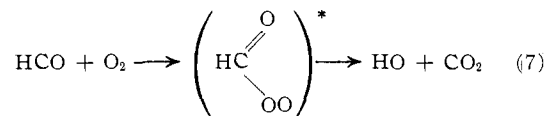$$\longrightarrow CH_3 + HCO \qquad (4)$$
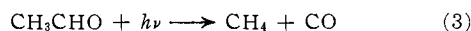
The quantum yield of (3) varies with wave length: 0.013 at 3130; 0.15 at 2804; and 0.28 at 2654 Å. Thus reaction 3 presumably contributes heavily to the destruction of acetaldehyde, but it does not contribute to the oxidations here studied—except as a nonobserved parallel reaction. Oxidation of methyl radical is believed to go by way of

$$CH_3 + O_2 \longrightarrow CH_3O_2{}^* \longrightarrow HO + CH_2O \qquad (5)$$

$$\overset{(M)}{\longrightarrow} CH_3OO \qquad (6)$$
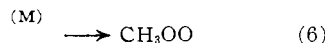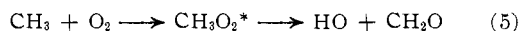
where HO is favored by high temperatures and low pressure and CH_3OO is favored by high pressure and low temperature. These studies were made at low temperature and low pressure and steps (5) and (6) are both important. The formyl radical HCO pre-

(9) F. E. Blacet and J. D. Heldman, *J. Am. Chem. Soc.*, **64**, 889 (1942); F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

sumably undergoes similar processes

$$HCO + O_2 \longrightarrow \left(HC\!\!\begin{array}{c} \nearrow O \\ \searrow OO \end{array}\!\! \right)^* \longrightarrow HO + CO_2 \qquad (7)$$

$$\overset{(M)}{\longrightarrow} HCO(OO) \qquad (8)$$

plus a direct bimolecular hydrogen atom abstraction

$$HCO + O_2 \longrightarrow HO_2 + CO \qquad (9)$$
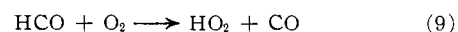
The concensus seems to be in favor of reaction 9 although there may be conditions favoring (7) or (8). As a part of the series of initial fast radical reactions, peroxy methyl radicals are believed to be converted to methoxy radicals

$$2CH_3OO \longrightarrow 2CH_3O + O_2 \qquad (10)$$
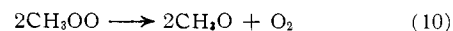
Thus one expects important amounts of the following radicals promptly to follow the primary photochemical reaction: CH_3OO, CH_3O, HO, HO_2, and perhaps $HCO(OO)$ and $HCOO$.

With six hydrogen-containing radicals one expects up to 36 different disproportionation reactions, but at most 12 different products. Many of these mathematical possibilities can be eliminated, but the mechanism seems to be quite inaccessible to any method that follows only products.

Even so, one or two quantitative statements can be made. The primary source of methyl peroxide is believed to be

$$2CH_3O \longrightarrow CH_3OOCH_3 \qquad (11)$$

but these same reactants also give a disproportionation reaction

$$2CH_3O \longrightarrow CH_2O + CH_3OH \qquad (12)$$
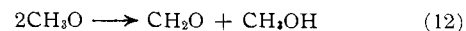
If reaction 11 is the primary source of peroxide and if (12) is the principal source of formaldehyde, the ratio of rate of formation of CH_2O and CH_3OOCH_3 should be constant

$$R_i(CH_2O)/R_i(CH_3OOCH_3) = k_{12}/k_{11} \qquad (13)$$

This relation is tested in Table IV. The relation is not particularly constant, but the significant thing is that the values 6.5 to 22 are the same order of magnitude as that found with methyl iodide (8.5 to 22). In the methyl iodide system, reaction 12 was regarded as the principal source of methanol, and the magnitude of the value for eq. 13 indicates that this reaction is the principal source of formaldehyde in the photooxidation of acetaldehyde.

If CH_3OOCH_3 is produced only by reaction 11, then the relative yield of methyl peroxide in various systems is a qualitative measure of the CH_3O radical abundance. Similarly CH_3OOH is formed only by abstraction of a hydrogen atom from other radicals by CH_3OO, and it is thus a qualitative measure of CH_3OO steady-state concentration. The average relative quantum yields are

Reactant	$\Phi(CH_3OOCH_3)$	$\Phi(CH_3OOH)$
CH_3I	0.037	0.12
CH_3CHO	0.011	0.21

Thus the steady-state concentration of CH_3O is suppressed relative to CH_3OO in this system.

Effects of γ-Radiation on the Surface Properties of Silica as Studied by the Infrared Spectra of Adsorbed Molecules

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The effect of γ-radiation on high area oxides has been mainly studied by indirect means. For example, the rate of H_2–D_2 exchange on silica has been shown to be markedly affected by radiation. The advent of infrared spectroscopy as a tool for the study of adsorbed molecules offers a more direct approach to studying the effect of radiation on surface properties. It is shown that dissociative ethylene chemisorption can be induced in silica by γ-radiation. Careful control experiments showed that no ethylene was adsorbed on the surface, without prior irradiation. The nature of the adsorbed species, the mechanism of growth of the adsorbed species, and the nature of the active sites induced by the radiation are discussed.

I. Introduction

While a considerable literature exists on the effect of radiation on the surface properties of oxides, direct measurements of these effects have been few. For instance, with regard to catalytic properties, many experiments have been reported[1-4] on the induced H_2–D_2 exchange activity due to γ-ray bombardment on a series of oxides. However, in most cases the oxides used had some activity before irradiation, and it is possible that the radiation had changed an already existing property of the oxides rather than having induced any new surface properties in the material. Another problem in the interpretation of H_2–D_2 exchange experiments is that it is unknown what particular surface property, or surface site, is responsible for the exchange. Hence, it is difficult to interpret the effect of radiation on exchange activity in terms of changes in the surface properties of the solid.

This point has been discussed by Taylor,[5] who has done a great deal of pioneering work in this field, and he had concluded "there is a basic difficulty in the characterization of defects that influence catalysis— namely, physical methods normally see features in the interior of the solid rather than on the surface simply because of the ordinarily much greater number of the former." However, there are exceptions to this rule. For instance, infrared spectroscopy can show directly the existence of some defects (such as OH groups) on the surfaces of oxides. It can also detect the presence of as little as $1/100$ of a monolayer of adsorbed hydrocarbons.[6]

The effect of irradiating silica, in vacuo, with Co^{60} γ-rays has been studied by measuring the infrared

spectra of molecules subsequently interacting with the irradiated surface. The majority of work has been done with ethylene. After evacuation of unirradiated silica, ethylene can be left for very long times above the surface, at room temperature, without adsorption. After irradiation, in marked contrast, adsorbed saturated species are very rapidly formed. This provides direct evidence that centers, very active for the strong chemisorption of unsaturated hydrocarbons, have been induced in this oxide by γ-radiation. Experiments to elucidate the nature of these sites, and their relation with the color centers[6] induced in silica, have been performed and are discussed in detail.

II. Experimental

(a) **Materials.**—Porous glass was obtained from the Corning Glass Works, by the courtesy of Dr. M. E. Nordberg. Tubular material, of varying radii but wall thickness of about 1 to 2 mm., was used, although some experiments were done with flat plates. In an attempt to ensure the maximum degree of uniformity of the samples, they were cut from 15-in. lengths of the tubing. In the preparation of porous glass, an acid-soluble component is leached out, leaving a silica matrix.[7] The thoroughness of this leaching determines, to a considerable extent, the impurities left on the surface of this material. Although the normal Na content of this material is about 400 parts per million (p.p.m.), we were able to obtain material with 50 p.p.m. of Na. In an effort to reduce the latter still further, we leached this material in boiling 1 N nitric acid for 15 hr., then rinsed most of the acid out, and stored the glass in distilled water.[8] An attempt was made to reduce the boron content of the material by leaching, calcining in air at a higher temperature than subsequently used, and then releaching.

Ethylene of 99.0% purity was supplied by the Matheson Co., East Rutherford, N. J. Specially purified ethylene was also used, supplied by the Phillips Petroleum Co., Bartlesville, Okla. This had a purity of 99.92%, and gas chromatographic analyses showed the main impurity to be a small amount of ethane. Hydrogen was obtained from the Linde Co., of Linden, N. J., and had a purity of 99.98%. Deuterium was supplied by the General Dynamics Corp., with a purity of 99.5%. Oxygen, NO, and Ar were supplied by the Matheson Co., with respective purities of 99.6, 99.0, and 99.99%. In the case of the noncondensable gases, they were dried by passage through traps at 77°K.

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