Table VI. 100-Ev Yields of Products in Irradiated D_2-CH_4-Xe Mixtures[a]

Run no.	Mole % CH_4	$G(CH_3D)$	$G(CH_2$-$D_2)$	$G(CHD_3)$	$G(CD_4)$	G(ethane)
			At 25°			
2b	1.54	1.00	0.14	0.11		
3b	3.06	0.62	0.25	0.10	0.06	
2a	6.2	0.43	0.21	0.09	0.05	0.076
5b	8.64	0.73	0.28	0.08	0.02	
3a	11.8	0.38	0.17	0.09	0.05	0.073
7b	15.9	0.39	0.32	0.10	0.03	0.087
			At −78°			
1b	1.54	0.36	0.18	0.11	0.07	<0.0
4b	3.6	0.75	0.19	0.10	0.05	
1a	6.2	0.65	0.30	0.22		
6b	8.6	1.55	0.32	0.03	<0.0	<0.0
8b	15.9	2.03	<0.0	<0.0		<0.0

[a] The a series experiments were performed at dose rate = 1.22×10^{13} ev/cc sec, and the b series experiments were performed at dose rate = 0.617×10^{13} ev/cc sec.

TD-D_2 (1:100)/Xe (50–58%)-CH_4 (1.5–16%) at 25 and −78° are presented in Table VI.

We observe that (1) ethane, propane, butane, and all deuterated methanes are formed initially at 25°, whereas, at −78° deuterated methanes are the only significant products, with CH_3D overwhelmingly predominant at higher CH_4 concentrations; (2) the higher hydrocarbons are destroyed at −78° at all CH_4 concentrations, whereas, the 100-ev yields of the more highly deuterated methanes are negative only above 6.2 mole % CH_4; (3) CH_3D yields are strongly dependent upon the CH_4 concentration at both 25 and −78°, but the proportionality is direct at −78° and inverse at 25°. On the basis of these observations it is apparent that Xe is incapable of inhibiting ionic reactions at Xe/CH_4 ratios in the range 40:1 to 4:1. It is also apparent that the proton–deuteron transfer sequence and other ionic reactions are responsible for the majority of products in these mixtures and that $XeD^+ + CH_4 \rightarrow CH_4D^+ + Xe$ cannot be ignored. It is not unlikely that Maschke and Lampe were correct in their assumption that the abstraction sequence is significant at the roughly 100-fold higher dose rates employed in their experiments at 25°, but ionic contributions must, if possible, be taken into account in the quantitative interpretation of their results.

Kinetics and Mechanism of the Gas Phase Reaction between Iodine and Formaldehyde and the Carbon–Hydrogen Bond Strength in Formaldehyde[1a]

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Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California. Received June 3, 1966

Abstract: The gas phase reaction of iodine with formaldehyde has been investigated spectrophotometrically in the temperature range 180–300°. The reaction is very clean, giving CO and HI as the only products except at very high conversions at the lowest temperatures, when a little CH_3I is formed as a side product. A reaction mechanism is presented in the text. Kinetic measurements over a wide range of initial conditions indicate that the rate-determining step is $I\cdot + CH_2O \rightarrow \cdot CHO + HI$, and log $k_4 = 10.92$–$17.43/\theta$, where $\theta = 2.303RT$ in kcal/mole. Further measurements of the inhibiting effect of HI on the reaction suggest that the back activation energy for step 4 is 1.5 kcal/mole. This difference in forward and back activation energies establishes a bond strength of $DH°_{298}$(H–CHO) = 87.0 kcal/mole. The value implies a dative π-bond energy in carbon monoxide of 68.5 ± 2 kcal/mole, in good agreement with other estimates.

Detailed studies of the kinetics of gas phase reactions of iodine with a variety of hydrocarbons have proved extremely fruitful in providing reliable values for many bond dissociation energies[2] and radical resonance energies.[3] Much of this work has been made possible by the development of a highly sensitive spectrophotometric technique,[2,3] which permits detection of as little as 10^{-3} torr of iodine and organic iodides in these systems.

Recently this work has been extended to reactions of iodine with oxygen-containing compounds.[4a] It has been shown that, as is the case with hydrocarbons, the reaction proceeds through the rate-determining step

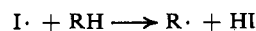$$I\cdot + RH \longrightarrow R\cdot + HI$$

(1) (a) This investigation was supported in part by Public Health Service Research Grant AP-00353-02 from the Air Pollution Division, Public Health Service. (b) Research Associate. Address correspondence to the Department of Chemistry, Reading University, Reading, Berkshire, England.

(2) (a) D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 4053 (1965); (b) D. B. Hartley and S. W. Benson, *J. Chem. Phys.*, **39**, 132 (1963); (c) P. S. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 2773 (1964); (d) M. Teranishi and S. W. Benson, *ibid.*, **85**, 2887 (1963).

(3) (a) K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964); (b) R. Walsh, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 650

(1966); (c) K. W. Egger and S. W. Benson, *ibid.*, **88**, 241 (1966); (d) A. S. Rodgers, D. M. Golden, and S. W. Benson, *ibid.*, **88**, 3194, 3196 (1966).

(4) (a) R. Walsh and S. W. Benson, *ibid.*, **88**, 650 (1966); (b) R. Klein and L. J. Schoen, *J. Chem. Phys.*, **29**, 953 (1958).

Table I. Product Distribution in the Gas Phase Reaction of I_2 with CH_2O

Temp, °K	Residence time, sec	Reactants[a]		[CO]	[HI]	Products[a]			Pressure change,[a]
		$[I_2]_0$	$[CH_2O]_0$	[CO]	[HI]	$[CH_3I]$	$[I_2]$	$[CH_2O]$	ΔP
543.0	4,000	2.81	7.61	2.79	5.29	0	0.18	5.0	2.6
481.5	10,400	3.16	74.5	2.80	5.32	0.16	0.44	68.4	2.4

[a] All pressures in torr.

the weakest hydrogen being abstracted. Under these circumstances, the bond strength $DH°(R-H)$ is readily obtained.

The present study, with formaldehyde as RH, was undertaken because the values for $DH°(H-CHO)$ and $\Delta H_f°(\cdot CHO)$ are subjects of some controversy. Klein and Schoen,[4b] for instance, have argued that $DH°(H-CHO) \leq 78$ kcal/mole since photodecomposition of CH_2O by a free-radical mechanism initiated by 3650-A radiation[5] cannot otherwise proceed. Early electron-impact studies[6] and a recent reinterpretation of the electronic spectrum of CH_2O[7] have suggested that $DH°(H-CHO) = 75 \pm 2.3$ kcal/mole, while further electron-impact data[8] give the value 79.5 kcal/mole. Calvert,[9] on the other hand, preferred a higher value of around 91 kcal/mole, which would be more consistent with mechanistic interpretations[5] of other aldehyde photolysis systems which require $E_a \cong 15$ kcal/mole for the step

$$M + HCO \longrightarrow \cdot H + CO + M$$

Furthermore, Calvert[10] has suggested that $DH°$ (CH_3CO-H) and $DH°(HCO-H)$ should be roughly equal, and the most recent value for the bond strength in CH_3CHO is 88 kcal/mole.[11] In addition, consideration of the role of formyl radical in dimethyl ether pyrolysis[12] support a value for $DH°(H-CHO)$ of 87 kcal/mole. It is hoped that the results reported here will clarify this situation somewhat.

Experimental Section

(a) Materials. Formaldehyde was prepared from Eastman Kodak paraformaldehyde by the method of Spence and Wild,[13] and stored at $-196°$. When required, it was warmed from this trap and handled in heated lines. Research grade resublimed iodine (Mallinckrodt) and anhydrous hydrogen iodide (Matheson) were used.

(b) Apparatus and Procedure. The apparatus and procedure have been described in detail in earlier publications.[3b,4a] Of the reaction products, hydrogen iodide and, when formed, methyl iodide were monitored spectrophotometrically. Carbon monoxide was identified as a product mass spectrometrically and separated as a noncondensable at $-196°$ (by adsorption on silica gel at $-196°$). In addition, iodine and formaldehyde were monitored spectrophotometrically. Rate measurements were restricted to initial rates except in the experiments where the inhibition by HI was examined. During these measurements, the monitoring light beam was periodically switched off in order to verify that the rates were not dependent on the light in any way. Although ultraviolet wavelengths were used, the light was of low intensity and

no effect of light on the rates was ever discerned. After preliminary experiments, the reaction vessel was treated with Dow-Corning 705 silicone oil (2% solution in CCl_4) when cold, in order to render it surface inactive.[14] After curing for 24 hr at 300°, the vessel suffered no loss in light transmittance at any wavelength.

Results

A series of preliminary experiments was carried out to establish the stoichiometry of the reaction. In these experiments the reaction was permitted to run to high conversion, final analysis being carried out for HI, CO, CH_3I, I_2, and CH_2O. The over-all pressure change was also measured. The results of two such experiments are shown in Table I.

It can be seen that, in the first listed experiment, the data can be fitted well by a stoichiometry of

$$I_2 + CH_2O \longrightarrow 2HI + CO$$
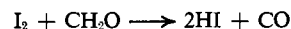
the material balances being extremely good. In the other listed experiment, a small quantity of CH_3I appears to have been formed at the expense of HI, and, in addition, the loss of CH_2O is rather larger than that of I_2. Detailed product–time curves for the above experiments revealed total iodine mass balances within $\pm 1\%$ throughout the runs, and, further, that the CH_3I found during the latter experiment only began to be formed beyond 50% conversion of I_2. Moreover, such experiments confirmed that no CH_3I was formed at all at temperatures greater than 512°K, and that it was only formed beyond 30–50% conversion of I_2 at temperatures in the range 450–480°K. No further examination of this secondary formation of CH_3I was carried out, except for one experiment in which HI and CH_2O (but no I_2) were mixed at 481°K and a very slow generation of CH_3I was indeed observed.

Rate measurements were confined to initial rates except in a few cases, and in these latter, conditions which could lead to formation of CH_3I were avoided. Rate measurements were interpreted in accordance with the followed mechanism which is a simple extension of that established for the reaction of I_2 with hydrocarbons[15]

$$M + I_2 \rightleftarrows 2I \cdot + M$$

$$I \cdot + CH_2O \underset{3}{\overset{4}{\rightleftarrows}} \cdot CHO + HI$$

$$\cdot CHO + I_2 \overset{2}{\longrightarrow} ICHO + I \cdot$$

$$\downarrow 5$$

$$HI + CO$$

The mechanism suggests the intermediate formation of formyl iodide (which decomposes into HI and CO and is too unstable to be observed). A steady-state

(5) R. Klein and L. J. Schoen, *J. Chem. Phys.*, **24**, 1094 (1956).
(6) R. I. Reed, *Trans. Faraday Soc.*, **52**, 1195 (1956).
(7) J. C. D. Brand and R. I. Reed, *J. Chem. Soc.*, 2386 (1957).
(8) T. W. Shannon and A. G. Harrison, *Can. J. Chem.*, **39**, 1392 (1961).
(9) J. G. Calvert, *J. Phys. Chem.*, **61**, 1206 (1957).
(10) J. G. Calvert, *J. Chem. Phys.*, **29**, 954 (1958).
(11) J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965).
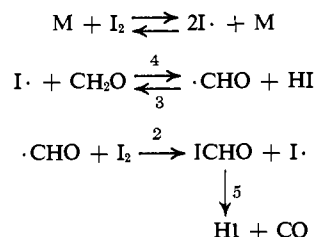(12) K. H. Anderson and S. W. Benson, *J. Chem. Phys.*, **39**, 1677 (1963).
(13) R. Spence and W. Wild, *J. Chem. Soc.*, 338 (1935).

(14) K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.*, **87**, 3314 (1965).
(15) S. W. Benson and H. E. O'Neal, *J. Chem. Phys.*, **34**, 514 (1961).

treatment of this mechanism gives the following rate expression

$$\left(\frac{d[I_2]}{dt}\right) = \frac{1}{2}\left(\frac{d[HI]}{dt}\right) = \frac{k_4 K_{I_2}^{1/2}[I_2]^{1/2}[CH_2O]}{1 + \dfrac{k_3[HI]}{k_2[I_2]}}$$

Experiments were designed to test this expression in two ways. (i) Initial rates were measured and fitted to

$$\frac{1}{2}\left(\frac{d[HI]}{dt}\right)_{t=0} = k_4 K_{I_2}^{1/2}[I_2]_0[CH_2O]_0$$

The results of these experiments are listed in Table II and it can be seen that the values obtained for k_4 are quite reproducible over a wide variation in the ratio

Table II. Kinetic Data for the Reaction
$I\cdot + CH_2O \longrightarrow \cdot CHO + HI$
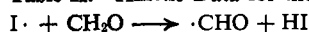
Temp, °C	$[I_2]_0$, torr	$[CH_2O]_0$, torr	$\dfrac{10^4}{2}\left\{\dfrac{d[HI]}{dt}\right\}_0$ torr/sec	$10^5 \times k_4 K_{I_2}^{1/2}$, torr$^{-1/2}$ sec^{-1}	$10^{-2}k_4$,[a] l./mole sec
179.9	10.93	61.4	0.542	0.0267	3.35
179.8	2.76	141.5	0.595	0.0253	3.17
179.8	25.8	25.6	0.346	0.0266	3.33
179.8	21.9	99.4	1.200	0.0258	3.24
182.4	1.08	151.8	0.523	0.0325	3.62
209.5	3.17	78.6	3.74	0.267	10.23
209.5	12.47	20.5	1.87	0.259	9.86
209.6	25.9	10.45	1.45	0.273	10.45
209.3	12.87	98.7	9.48	0.268	10.26
208.7	3.16	98.2	4.49	0.257	10.09
208.9	1.15	80.2	2.23	0.259	10.16
239.4	1.57	96.5	27.0	2.23	29.7
239.4	20.8	39.5	42.4	2.35	31.3
239.5	5.37	52.1	27.9	2.32	30.7
238.9	2.70	49.7	18.1	2.22	30.1
238.9	19.8	6.76	7.34	2.44	33.0
238.9	3.36	5.27	2.09	2.16	29.3
240.6	1.12	50.8	13.55	2.52	32.0
239.0	2.20	22.5	7.44	2.23	29.9
268.9	1.03	11.71	16.9	14.2	75.5
269.4	17.64	1.09	7.04	15.4	80.5
270.0	1.06	10.09	16.9	16.3	83.8
270.1	9.53	3.34	16.9	16.4	84.3
270.1	3.02	5.82	15.9	15.7	80.7
270.9	14.87	1.09	7.21	17.2	86.1
269.8	2.81	7.61	19.7	15.4	79.8
269.8	1.09	6.09	10.17	16.0	82.8
270.0	10.76	40.1	204	15.5	79.6
299.7	0.915	4.82	36.5	79.1	177.8
301.1	5.54	0.80	15.9	84.4	182.8

[a] In calculating k_4, K_{I_2} (equilibrium constant for $I_2 \rightleftarrows 2I\cdot$) was computed from JANAF tables.[17]

[CH₂O]/[I₂]. It should be noted that the reaction vessel S/V ratio was not varied during these experiments, but preliminary data (not recorded) obtained in an unconditioned vessel showed some variability of apparent k_4 values at the lowest temperatures (precisely analogous to that attributed to surface effects in earlier work[4a]). These effects were completely suppressed when the vessel was treated in the manner already described, and it was therefore assumed that the rates quoted here do not include any heterogeneous component of reaction.

(ii) Experiments were performed with added HI and the data fitted to

$$\frac{[HI]}{[I_2]} = \frac{k_2}{k_3}k_4 K_{I_2}^{1/2}\frac{[CH_2O]}{\left(2\dfrac{d[I_2]^{1/2}}{dt}\right)} - \frac{k_2}{k_3}$$

Good straight lines were obtained when [HI]/[I₂] was plotted against [CH₂O]/(2 d[I₂]$^{1/2}$/dt). An example of such a plot is shown in Figure 1. It was found that the inhibition constant, k_3/k_2, was very small and therefore difficult to measure accurately. The most reliable values were obtained when a high initial ratio of [HI]/[I₂] was used and the plots were constrained to pass through the point on the abscissa corresponding to the previously determined value of $[k_4 K_{I_2}^{1/2}]^{-1}$. In these cases the error in k_3/k_2 was estimated to be not more than ±5%. Unfortunately, at 480 and 455°K the limitation imposed by secondary formation of CH₃I meant that HI could not be added initially, and the accuracy of the method was considerably reduced to a ±20% error in k_3/k_2. The values of k_3/k_2 obtained in this way are listed in Table III.

Table III. Kinetic Data for Inhibition by HI

Temp, °C	$[I_2]_0$ torr	$[CH_2O]_0$ torr	$[HI]_0$ torr	$10^5 k_4 K_{I_2}^{1/2}$, torr$^{-1/2}$ sec^{-1}	k_3/k_2[a]
182.4	1.08	151.8	...	0.0325	0.0478 ± 0.0080
208.7	1.15	80.2	...	0.257	0.0400 ± 0.0070
240.6	1.025	102.6	21.3	2.40[b]	0.0461 ± 0.0022
270.8	1.12	51.5	20.8	16.3[b]	0.0452 ± 0.0021
299.5	1.11	30.0	20.3	82.5[b]	0.0499 ± 0.0024

[a] Errors estimated from experimental uncertainties. [b] These values estimated from Arrhenius plot in Figure 2.

Arrhenius plots for both k_4 and k_3/k_2 were made and these are shown in Figures 2 and 3. The least-mean-squares fit for k_4 was extremely good and measurements of the slope and intercept gave

$$\log k_4 \text{ (l./mole sec)} = 10.92 \pm 0.04 - \frac{17.43 \pm 0.09}{\theta}$$

(The small errors are probably somewhat fortuitous, and a more realistic appraisal of the uncertainties would put a limit of ±0.2 kcal/mole on E_a.)

In making the Arrhenius plot for k_3/k_2, there was not sufficient data to warrant a least-mean-squares fit, and the line shown was fitted by eye. The parameters obtained from this line were

$$\log (k_3/k_2) = -0.95 \pm 0.40 - \frac{0.93 \pm 0.93}{\theta}$$

The value for $E_3 - E_2 = 0.9$ kcal/mole is in good agreement with similar values in other systems[2,15] where radicals compete for HI and I₂; in particular[16] for the acetyl radical, $E_3' - E_2' = 1.5 \pm 1.0$ kcal/mole where these activation energies refer to the reactions

$$CH_3\dot{C}O + HI \xrightarrow{3'} CH_3CHO + I\cdot$$

$$CH_3\dot{C}O + I_2 \xrightarrow{2'} CH_3COI + I\cdot$$
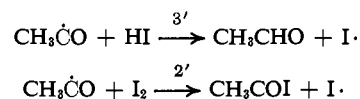
Radical reactions with iodine are known to be extremely fast, and it seems reasonable to assume that their

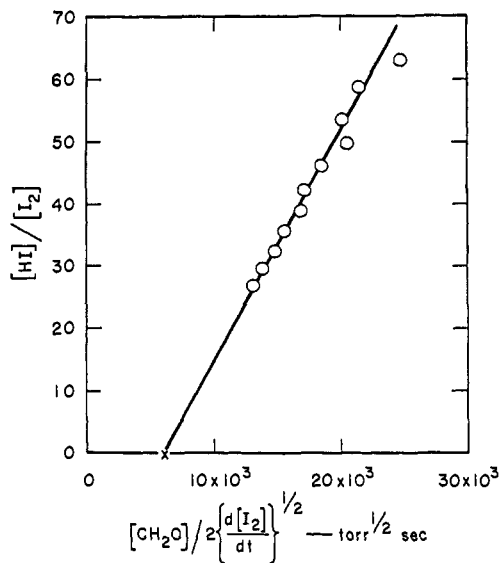(16) H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **37**, 540 (1962).

Figure 1. Plot showing effect of added HI. The line is constrained to pass through point marked ×.

Figure 2. Arrhenius plot for the rate constant k_4.

Figure 3. Arrhenius plot for inhibition constant k_3/k_2. Flags on points indicate estimated error limits.

activation energies lie in the range 0–1 kcal/mole. A value of $E_3 = 1.5 \pm 1.0$ kcal/mole is therefore consistent with this assumption.

Thus, $\Delta H°_{4,3}(513°K) = E_4 - E_3 = 17.4 - 1.5 = 15.9 \pm 1.0$ kcal/mole. When corrected to room temperature using listed C_P values,[17] $\Delta H°_{4,3}(298°K) = 15.7 \pm 1.0$ kcal/mole is obtained. Using the formulas

$$\Delta H_f°(\cdot CHO,g) = \Delta H°_{4,3} - \Delta H_f°(HI,g) + \Delta H_f°(CH_2O,g) + \Delta H_f°(I\cdot,g)$$

and

$$DH°(H-CHO)_{298} - DH°(H-I)_{298} = \Delta H°_{4,3}(298°K)$$

and the tabulated heats of formation,[17] the following values were calculated: $\Delta H_f°(\dot CHO,g) = +7.2 \pm 1.8$ kcal/mole and $DH°(H-CHO)_{298} = 87.0 \pm 1.0$ kcal/mole.

The dative bond formed by donation of a lone pair of electrons from oxygen to carbon in carbon monoxide accounts for the weakness of the C–H bond in CHO. From the above data, it may be calculated that $DH°(H-\dot CO)_{298} = 18.5 \pm 1.8$ kcal/mole. The dative bond energy $DH°(CO\pi)$ may be defined by

$$DH°(CO\pi) = DH°(R-COR)_{298} - DH°(R-\dot CO)_{298}$$

Its value for the case R = H is thus $87.0 - 18.5 = 68.5 \pm 2$ kcal/mole. The significance of such a number rests in its generality. Similar estimates may be obtained for the cases R = CH_3, R = Cl. They are 70 ± 2 kcal/mole and 70 ± 3 kcal/mole, respectively,[18] indicating that such estimates are, within experimental error, independent of R. The implication is that any energies of interaction between R groups in R_2CO, or between an R group and an electron in R–CO, cancel.

Discussion

(a) Mechanism. The reaction under study has a very clear-cut stoichiometry apart from the slow second-

(17) "JANAF Interim Thermochemical Tables," D. R. Stull, Ed., Dow Chemical Co., Midland, Mich., 1963.

(18) The $\Delta H_f°$ values used in these estimates were taken from: (a) S. W. Benson, *J. Chem. Educ.*, **42**, 502, (1965); (b) W. G. Burns and F. S. Dainton, *Trans. Faraday Soc.*, **48**, 39 (1952).
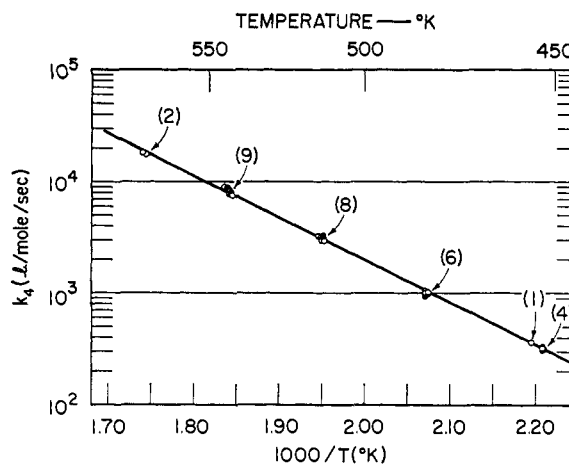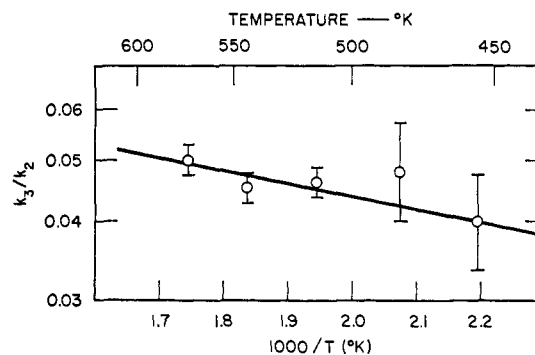
ary reaction leading to formation of CH_3I at low temperatures and high conversions. A reasonable mechanism has been proposed and shown to be consistent with the kinetic results. Moreover, the Arrhenius A factors, which have been obtained, are characteristic of these reactions.[2,15] A theoretical calculation of A_4, based on a transition-state model,[19] predicts a value of $10^{10.9}$ l./mole sec, in precise agreement with the observed value. The ratio A_3/A_2 has the value 0.11 (+0.17, −0.07), very similar to that for A_3'/A_2' of 0.34 $\pm$ 0.25 for the analogous reactions of the acetyl radical.[16]

The alternative steps

$$M + \cdot CHO \xrightarrow{6} \cdot H + CO + M$$

$$H\cdot + I_2 \xrightarrow{7} HI + I\cdot$$
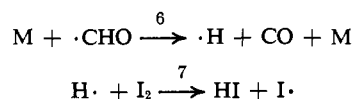
were not included in the mechanism on the grounds that step 6 is 18.5 kcal/mole endothermic and could not possibly compete with step 2, a reaction with essentially no activation energy (despite possible A factor differences). This consideration also rules out reaction 6 in aldehyde photolyses, where iodine has been used as a radical scavenger. Calvert and Pitts[20] have suggested the formation of the unstable formyl iodide by reaction 2 in aldehyde photolyses, in the presence of iodine.

(19) A. S. Rodgers and S. W. Benson, to be published.

(20) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 602.

The postulate, here, of intermediate formation of formyl iodide is consistent in general with the products of I_2 + RH systems.[2,3] Formyl iodide has never been prepared to our knowledge and we would certainly expect it to be thermodynamically unstable, with respect to decomposition, to HI and CO. The absence of detectable ICHO merely implies that step 5 is fast. Indeed, from an estimate of the maximum pressure of ICHO, which could have existed in the reaction vessel without giving rise to serious inconsistencies in absorbance (provided a reasonable absorption coefficient is assumed), the following lower limit can be estimated: $k_5 \geq 6.6 \times 10^{-2}$ sec^{-1} (540°K). Step 5 could be heterogeneous, but if it were not, and the mechanism proceeded *via* a three-center transition state, rough limits could be placed on the Arrhenius parameters. From a set of empirical rules derived from transition-state calculations,[21] we estimate an A factor of $10^{13.7}$ for such a path at the high-pressure limit. If step 5 is identified with such a path, it can be calculated that $E_5 \leq 37$ kcal/mole, provided the reaction occurs at its high-pressure limiting rate. It is exceedingly likely that such a unimolecular reaction would be in its fall-off region of pressure dependence, in which case one might expect the upper limit on E_5 to be even less. In view of the paucity of data on three-center elimination reactions, such estimates are clearly important. In this connection, it is relevant to note that the analogous elimination of HF from FCHO appears to be heterogeneous.[22]

Any over-all back-reaction (of HI with CO) can be rejected on thermodynamic grounds (the equilibrium constant for the reaction predicts complete conversion to products). For the above reasons, we feel that the proposed mechanism is essentially correct and complete.

(b) The Bond Dissociation Energy $DH°(\text{H–CHO})$ and the Heat of Formation $\Delta H_f°(\cdot\text{CHO})$. The values obtained in this work, *viz.*, $DH°(\text{H–CHO}) = 87.0$ kcal/mole and $\Delta H_f°(\cdot\text{CHO}) = 7.2$ kcal/mole, are clearly in conflict with estimates of several previous workers. However, Calvert's suggestion[10] that aldehydric C–H bonds are roughly equal is well borne out. Moreover, the present results are in approximate agreement with values derived from studies of aldehyde photolyses,[9] suggesting that the step, M + HĊO → M + ·H + CO, is probably rate determining in those systems, but that some small positive activation energy may be involved in termination. The formyl radical decomposition also occurs during the pyrolysis of dimethyl ether[12] with an activation energy of 23 kcal/mole (780°K). If combined with the not unreasonable back activation energy of 2 kcal/mole, the over-all heat change at 780°K is in precise agreement with the value predicted from this work. A more straightforward study of formyl radical decomposition or, alternatively, a study of the reaction of hydrogen atoms with CO would clarify this point.

We cannot offer a specific explanation as to why the electron impact values[6,8] are low, but we feel that ion-molecule reactions in a mass spectrometer are generally less well understood than the radical reactions in our present system.
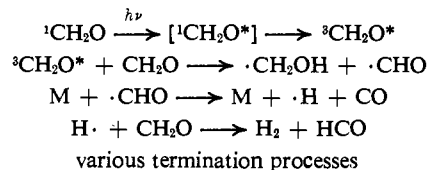
If the results of this work are correct, the most

(21) S. W. Benson and H. E. O'Neal, to be published.
(22) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, 16, 397 (1965).

interesting unexplained observation is that of Klein and Schoen[5] who were able to photolyze mixtures of CH_2O and CD_2O, with 3650-A radiation and obtain large quantities of HD, thus indicating a free-radical mechanism. This wavelength, which corresponds to 78.3 kcal/mole, is insufficient to break the C–H bond.

A possible explanation of this result could be a mechanism, initiated by an excited state of CH_2O, possibly a triplet, as follows.

$$^1CH_2O \xrightarrow{h\nu} [^1CH_2O^*] \longrightarrow {}^3CH_2O^*$$
$$^3CH_2O^* + CH_2O \longrightarrow \cdot CH_2OH + \cdot CHO$$
$$M + \cdot CHO \longrightarrow M + \cdot H + CO$$
$$H\cdot + CH_2O \longrightarrow H_2 + HCO$$

various termination processes

Excited state molecules are known to react chemically with oxygen,[23] and recently O'Neal and Larson[24] have succeeded in measuring the rate of a trapping reaction of an excited triplet state of $(CH_3)_2CO$ by HBr, during acetone photolysis. The Arrhenius parameters[24] for this reaction, which eventually results in isopropyl alcohol formation, were $10^{9.6}10^{1.1/\theta}$, indicating that the triplet state of acetone is somewhat more reactive than methyl radicals.

If a mechanism, such as the above, is correct, CH_3OH might be expected among the products as a result of either an abstraction or disproportionation reaction of $\cdot CH_2OH$. Methyl alcohol has never been reported as a product in the photolysis of CH_2O, although it is not clear whether analysis for it has ever been performed. It is a known product of CH_2O pyrolysis.[25] If it were formed in significant quantities during photolysis, an excess of CO over H_2 would result. In a recent high-temperature photolysis at 3655 A by Venugopalan and Kutschke,[26] the results do show such an excess. On the other hand, CH_3OH does not appear to be a product in the flash photolysis of CH_2O.[27]

Spectroscopic evidence is not inconsistent with such an interpretation of the photolysis. Formaldehyde has an excited $^1A_2$ state at 80.6 kcal/mole above the ground state ($^1A_1$),[7] and detailed spectral analysis[28] shows that photolysis by 3650 A would populate levels at slightly in excess of 82 kcal/mole above the ground state. (Vibrational energy provides the 4 kcal/mole in excess of the photon energy.) Furthermore, there is a predissociation at 82.1 kcal/mole from the $^1A_2$ state, and it is known tht the $^3A_2$ lies slightly below it in energy. Indeed, absorption bands at 3619 and 3705 A have been assigned to direct $^1A_1 \rightarrow {}^3A_2$ transitions,[28] the triplet in each case being vibronically excited. The triplet has never been seen in emission, and so its lifetime is not known, but if it is lost through a trapping reaction, the predissociation from the $^1A_2 \rightarrow {}^3A_2$, and the photolysis, are explained.

It is evident that formaldehyde photolysis is somewhat more complicated than was hitherto suspected.

(23) G. B. Porter, *J. Am. Chem. Soc.*, 79, 8178 (1957).
(24) C. W. Larson and H. E. O'Neal, *J. Phys. Chem.*, 70, 2475 (1966).
(25) J. E. Longfield and W. D. Walters, *J. Am. Chem. Soc.*, 77, 6098 (1955).
(26) M. Venugopalan and K. O. Kutschke, *Can. J. Chem.*, 42, 2451 (1964).
(27) R. D. McQuigg and J. G. Calvert, Symposium on Structure and Photochemistry of Excited States, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.
(28) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, 36, 31 (1958).

It is exceedingly likely that the pyrolysis and oxidation are similarly complex systems, and we feel that they could be profitably reexamined in the light of the results of this work.

The Absolute Rate of the Reaction between Excited Mercury Atoms ($^3P_1$) and Ethylene, and the Role of Imprisonment of Resonance Radiation in Fluorescence Experiments

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Abstract: The rate constant (k) of an energy-transfer reaction, $Hg(^3P_1) + C_2H_4 \rightarrow Hg(^1S_0) + C_2H_4^*$, is determined by measuring the decrease in the intensity of fluorescence, $Hg(^3P_1) \rightarrow Hg(^1S_0) + h\nu$, as a function of ethylene pressure. Quenching data are extrapolated to zero pressure of mercury to eliminate the effect of the imprisonment of resonance radiation. At 25°, k_q is found to be 2.48×10^7 mm^{-1} sec^{-1}, corresponding to a quenching cross section of 48.2 Å^2. When mercury pressure, p (mm), is appreciable, the mean life, τ, of the excited state, estimated by using the Stern–Volmer equation, increases with increasing p according to the relation, $\tau = \tau_0 (1 + 0.25 \times 10^4 p\rho) (p \lesssim 4 \times 10^{-4})$, where $\tau_0 (= 1.08 \times 10^{-7}$ sec) is the mean life of an isolated atom and ρ is the distance in centimeters from the irradiated slab of mercury to the emerging surface of a cell. A diffusion model for the transport of resonance radiation yields the relation $\tau = \tau_0(1 + 0.28 \times 10^4 p\rho)$, which agrees well with experiments.

The quenching of $Hg(^3P_1)$ atoms by various gases plays an important role in the elucidation of structural factors which govern the efficiency of electronic energy transfer.[1] The rates of this quenching can be determined by using the Stern–Volmer equation[2]

$$\frac{Q}{Q_0} = \frac{1}{1 + \tau k_q[M]} \qquad (1)$$

where Q and Q_0 denote the intensity of fluorescence, $Hg(^3P_1) \rightarrow Hg(^1S_0) + h\nu$, in the presence and absence of M, and τ is the mean life of the excited state.[3] Quenching data provide τk_q, from which k_q can be estimated, if τ is known. Essentially, this is the method used in the past to determine absolute quenching rates. It is called a physical method, to distinguish it from a chemical method[4] which is often used to determine relative quenching rates. The mean life, τ_0, of an isolated atom is 1.08×10^{-7} sec. In practice, however, appreciable mercury vapor is always present and this greatly complicates the estimation of τ to be used in (1).

The ground-state atoms have a very high absorption coefficient for resonance radiations.[5] For this reason, a photon emitted as fluorescence usually undergoes several absorption–emission processes before it reaches

the emerging surface of a cell. Since a photon can be quenched as long as it resides within a cell, the net effect of the above phenomenon, known as imprisonment, is to prolong τ. Thus τ depends both on mercury pressure and on cell geometry. Several theories[6] have been advanced to treat the imprisonment, and the resulting theoretical τ is then used to evaluate k_q from quenching data.[7] Therefore, various assumptions and approximations involved in the theory of imprisonment are inevitably incorporated in presently accepted k_q values.

The major source of error in the theoretical estimation of τ seems to be the idealization of cell geometry. A typical experiment for the investigation employs a flat disk of thickness 1.3 cm and of diameter 5.1 cm. In the theory, such a cell is assumed to be an infinite slab so that the transport equation can be reduced to one dimension. Theoretical τ values estimated on the basis of this idealization agree with experiments only in the order of magnitude.[5,8]

To obtain reliable quenching rates and also to test the theory of imprisonment as applied to the quenching rate calculations, then, it is highly desirable to determine k_q without using a theoretical τ value. This is attempted in the present work.

Since the imprisonment prolongs τ, τk_q estimated from (1) should increase with increasing pressure, p, of

(1) For example, see (a) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," The Cambridge University Press, Cambridge, 1961; (b) R. J. Cvetanović, *Progr. Reaction Kinetics,* 2, 39 (1964); (c) H. E. Gunning and O. P. Strauz, *Advan. Photochem.,* 1, 209 (1963).

(2) O. Stern and M. Volmer, *Z. Physik,* 20, 183 (1919); also see ref 1a.

(3) More properly, τ here should be called an "apparent" or "imprisonment" lifetime. The meaning of τ will be further clarified in the subsequent discussion.

(4) R. J. Cvetanović, *J. Chem. Phys.,* 23, 1208 (1955).

(5) T. Holstein, *Phys. Rev.,* 72, 1212 (1947).

(6) For a review, see ref 5.

(7) M. W. Zemansky, *Phys. Rev.,* 36, 919 (1930).

(8) Actually, the quantity concerned in the investigation of the imprisonment is the decay time of imprisoned resonance radiation, after the exciting beam is cut off. Under experimental conditions commonly used in quenching experiments, where the Stern–Volmer equation is approximately valid, the decay time and τ are the same; hence no attempt is made in the present paper to distinguish between them.