[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Photo-decomposition of Formic Acid Vapor

BY EVERETT GORIN AND HUGH S. TAYLOR

The photo-decomposition of formic acid vapor is of interest because it is known to yield two sets of products (a) carbon monoxide and water and (b) carbon dioxide and hydrogen. Data have been obtained hitherto by Ramsperger and Porter[1] for the full radiation of a hot mercury arc and by Bates and Taylor[2] for the mercury sensitized reaction. In these cases the percentage decomposition to form carbon monoxide and water varied from 68 to 76, respectively. Herr and Noyes[3] have reported a quantum yield corresponding to 0.52 molecule uncondensed in liquid air per quantum of unfiltered mercury radiation. We have examined the nature of the products as a function of the extent of the association of the vapor as double molecules, and of the wave length employed. We have also ascertained the quantum yield in the decomposition of both species. To elucidate the reaction mechanism we have studied the primary photo-process in presence of para-hydrogen as an indicator of the presence of atomic hydrogen.

Experimental Data

A. Dynamic Experiments.—The preliminary work to ascertain the nature of the reaction products as a function of the association of formic acid was carried out, by a flow method, in a modified form (Fig. 1) of the apparatus described by Bates and Taylor,[2] in which photo-decomposition occurred during passage of the formic acid vapor through a water-heated quartz reaction system surrounded by a low pressure mercury arc, described by the same authors. Since such an arc is rich in resonance radiation, it was necessary carefully to exclude mercury from the reaction zone, which was protected from manometer and pump systems by liquid air traps F and H.

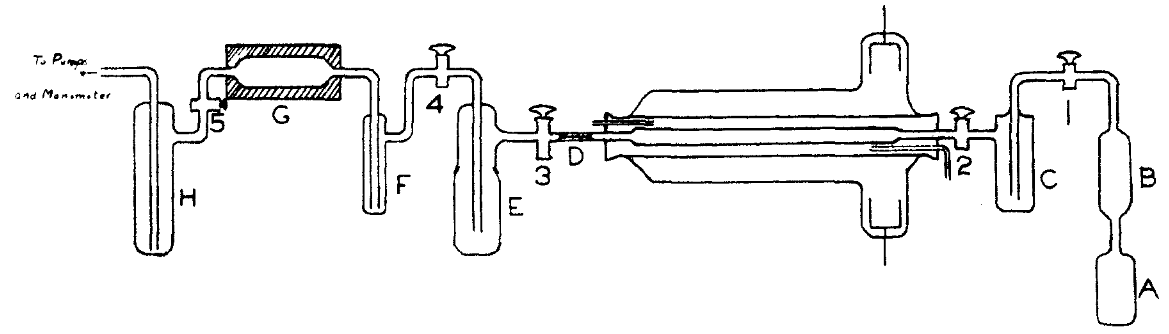


Fig. 1.—Photo-decomposition of formic acid vapor, apparatus for dynamic experiments.

The formic acid used was in all cases a c. p. grade, dried over calcium chloride. It was alternately frozen in a carbon dioxide–ether mixture, evacuated in a mercury-oil pump combination and then thawed, the process being repeated several times until no more bubbles of gas formed in the liquid. It was then vacuum distilled from A into the reservoir C connected directly with the quartz reaction vessel. The purity of the resultant product was demonstrated by the concordance of its vapor pressures with the data of Coolidge.[4]

Procedure.—With stopcock 2 closed the arc was started and the reaction temperature adjusted by means of the water circulating through the water jacket. When the temperature became constant the traps H, F and E were immersed in liquid air, the copper oxide tube G heated to 325 ± 25° and all stopcocks opened. After about thirty minutes of operation the arc was turned off and the products collected and analyzed as follows. The vessel C which had been maintained at room temperature during the run was cooled in carbon dioxide–ether and all gases removed by pumping. The carbon dioxide, formic acid vapor and water vapor condensed in E, which had a ground-glass joint to facilitate subsequent cleaning. The carbon monoxide and hydrogen were burned to carbon dioxide and water in G and condensed in H. With stopcock 5 closed the combined pressure of these products was measured on a mercury manometer. By surrounding H with carbon dioxide–ether, the carbon dioxide present in the combustion products could be removed by pumping and then the pressure of the remaining water vapor could be measured separately and then removed. Next the liquid in E was thawed out, carbon dioxide–ether placed around the trap and the carbon dioxide distilled to H where its pressure was measured. The relative amounts of carbon monoxide, hydrogen and carbon dioxide were thus readily determined. In the last three runs water vapor pressure was also measured.

To ensure absence of mercury vapor in the reaction sys-

---

[1] Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926).

[2] Bates and Taylor, *ibid.*, **49**, 2438 (1927).

[3] Herr and Noyes, *ibid.*, **50**, 2345 (1928).

[4] Coolidge, *ibid.*, **50**, 2166 (1928).

tem the apparatus, from 1 to 4, was cut down after runs 6 and 11 and cleaned with fuming nitric acid. The decomposition rate was not changed thereby, which indicates that the true photochemical reaction was being measured.

Experimental Results.—The data of 17 runs are shown in Table I. In the last three runs the reaction zone from 2 to 3 was filled with vapor at 35 mm. pressure and then irradiated for twelve hours to complete decomposition.

TABLE I

PRODUCTS OF PHOTO-DECOMPOSITION OF FORMIC ACID VAPOR

	Temp., °C.	% CO_2	% H_2	% CO	% H_2O
1	32.2	47.2	47.0	2.9	2.9
2	32.0	49.5	50.5	0	0
3	33.0	48.5	48.0	1.7	1.7
4	29.2	49.2	50.8	0	0
5	37.6	50.2	49.8	0	0
6	32.0	43.5	43.7	6.4	6.4
7	80.5	26.0	28.2	22.9	22.9
8	29.0	49.0	50.9	0.05	0.05
9	30.9	46.2	41.8	6.0	6.0
10	100	23.2	24.3	26.2	26.2
11	100	23.0	23.6	28.2	28.2
12	100	23.0	24.2	26.4	26.4
13	100	22.2	22.2	28.3	28.3
14	70	33.0	34.4	16.3	16.3
15	60	36.3	37.5	13.1	13.1
16	55	41.6	42.1	8.1	8.1
17	55	40.5	40.9	8.3	8.3
18	70	34.6	34.6	15.4	15.4

Discussion.—From the measurements of Ramsperger and Porter[1] and of Coolidge[4] of the vapor density it follows that at pressures greater than 10 mm. and temperatures below 30° the double molecule is the predominant species. The data of Table I show that these molecules decompose practically exclusively to carbon dioxide and hydrogen.

The fractions of light absorbed by the double and single molecules are obviously $\alpha_1 P_b/(\alpha_1 P_b + \alpha_2 P_m)$ and $\alpha_2 P_m/(\alpha_1 P_b + \alpha_2 P_m)$ where P_b and P_m are the pressures of the bimolecular and unimolecular species, α_1 and α_2 their coefficients of absorption according to Beer's Law. From the mass law expression $P_m^2/P_b = K$ the fraction of light absorbed by the double molecules at pressure P is

$$\frac{2P + K - \sqrt{4PK + K^2}}{2P + K - \sqrt{4PK + K^2} + (\alpha_2/\alpha_1)(\sqrt{4PK + K^2} - K)}$$

Assuming strict additivity of decomposition of both species, identical quantum yields (see later), and the relative probabilities X and Y of decomposition of the single species to produce, respectively, $(CO + H_2O)$ and $(CO_2 + H_2)$, we derive at once an expression for the fraction ϕ_1 forming $(CO + H_2O)$ as a function of the pressure, *viz.*

$$\phi_1 = \frac{X(\alpha_2/\alpha_1)(\sqrt{4PK + K^2} - K)}{(2P + K - \sqrt{4PK + K^2}) + (\alpha_2/\alpha_1)(\sqrt{4PK + K^2} - K)} \tag{1}$$

We choose for the pressure a value of 15 mm. Actually in the flow runs it varied along the reaction zone from C to the capillary D. However, since at 100° single molecules largely predominate ($K_p = 269$ for P in mm.), the result will not be very sensitive to pressure. This gives for the probabilities X and Y the values 0.69 and 0.31, respectively.

For complete decomposition, as in the last three runs, we can take a mean value of equation (1)

$$\phi_1 = \frac{X(\alpha_2/\alpha_1)}{P} \int_0^P \frac{(\sqrt{4PK + K^2} - K)\mathrm{d}P}{(2P + K - \sqrt{4PK + K^2}) + (\alpha_2/\alpha_1)(\sqrt{4PK + K^2} - K)}$$

Introducing a new variable $\sqrt{4PK + K^2} = y$, $K^2(1 + 2\alpha_2/\alpha_1) = c$ and $2K((\alpha_2/\alpha_1) - 1) = b$ this integral may be evaluated.

$$\phi_1 = \frac{X}{P}\frac{\alpha_2}{\alpha_1}\left\{\sqrt{4PK + K^2} - \frac{K + b}{2} \log (4PK + K^2 + b\sqrt{4PK + K^2} + c) + \frac{b^2 - b - 2c}{4c - b^2} \tan^{-1} \frac{2\sqrt{4PK + K^2} + b}{\sqrt{4c - b^2}} - K + \frac{K + b}{2} \log (K^2 + bK + c) - \frac{b^2 - b - 2c}{4c - b^2} \tan^{-1} \frac{2K + b}{\sqrt{4c - b^2}}\right.$$

From the two final experiments at 55° where $K = 20.4$ and $P = 35$ mm. the value of $X = 0.70$. In the last experiment at 70° where $K = 56.6$ and $P = 35$ mm., the value of X is 0.72. These values are in agreement with the experimental results.

We conclude, therefore, that, whereas the double molecules yield only carbon dioxide and hydrogen, the single molecules give the following decomposition products: 34.5% CO; 34.5% H_2O; 15.5% CO_2; 15.5% H_2.

B. Static Experiments.—In experiments with approximately monochromatic light sources, for an examination of products and quantum yields, a static system was employed.

Apparatus.—Two reaction cells were employed, one a Pyrex tube, 50 cm. long, 40 mm. in diameter, fitted with a quartz window sealed on with hard de Khotinsky cement. For shorter wave length experiments and the quantum yield measurements a cylindrical fused quartz cell, with plane windows, 14 cm. long and 4.5 cm. diameter was used. In the first instance, temperature was controlled by an external water-bath, in the latter by an electric resistance furnace. The pump system consisted of a Cenco Hi-Vac oil pump in series with two mercury diffusion pumps. Two manometers were used to measure the pressure of formic acid vapor, in the earlier work a butyl phthalate manometer and later a mercury manometer. A McLeod gage with a pressure range from 0.1 to 10^{-6} mm. served to measure the pressure of products.

Analysis.—After exposure, the formic acid was frozen out along with carbon dioxide and water in liquid air and the residual pressure ($CO + H_2$) was read on the McLeod gage. This gas was then pumped off, the liquid air replaced by carbon monoxide–ether mixture and the pressure of carbon dioxide measured. The pressures measured were of the order of 10^{-2} to 10^{-3} mm. The consistency of the results obtained in both static and dynamic systems is our reason for believing that these results contain but small errors.

Light Sources.—The sources used were a hot mercury arc, zinc, cadmium and aluminum sparks. We employed with advantage as a steady spark source the form described by Wiig and Kistiakowsky.[5] The focal insolation method was adopted for obtaining approximately monochromatic light. A single condensing lens was used to focus the light source. The spherical aberration was reduced to a minimum by blocking out two-thirds of the lens surface, the portion between 0.75 *r* and 0.91 *r* being used for reasons of maximum homogeneity and because of the large angle the refracted rays make with the axis, thus facilitating wave-length separation. The position of the diaphragm and the most convenient size of opening were determined by calculation and experimental test using the spectrograph. While this improved the working conditions the isolation of a particular wave length was not complete due to diffraction around the edges of the blocking disks. The fraction of total intensity due to the group required was probably 98% of the total. The centers of gravity of the various wave lengths used were: Al spark, 1900 Å.; Zn spark, 2090 Å.; Cd spark, 2140 Å.; Zn spark, 2540 Å. In the case of aluminum the group at 1860 Å. and the lines at 1960 and 1990 Å. were about equally rich. Isolation of the zinc lines at 2540 Å. was not complete, longer wave lengths being present. For the experiments with longer wave lengths than 2500 Å. the light coming through the monochromator was passed through a quartz cell containing a dilute aqueous solution of formic acid. This cuts out radiation of wave lengths below 2400 Å. and so enhances the accuracy of the experiments with the much more feebly absorbed radiation above 2500 Å.

Determination of Quantum Yield.—Light passing through the cell was focused on the surface of a Moll large-surface thermopile connected to a Leeds and Northrup galvanometer. The whole apparatus was grounded and shielded against external electrical disturbances. The thermopile, which was fairly uniformly sensitive over the various areas, was calibrated with a Bureau of Standards lamp. Suitable corrections were made for absorption due to the rear window of the cell and for the quartz window of the thermopile. The whole experimental arrangement for quantum yield measurements was calibrated by determining the quantum yield for the hydrogen bromide decomposition.

TABLE II

PRODUCTS OF PHOTO-DECOMPOSITION OF FORMIC ACID VAPOR. INFLUENCE OF TEMPERATURE, PRESSURE AND WAVE LENGTH

Temp., °C.	Light source	Mean wave length in Å.	Pressure HCOOH in mm.	$CO + H_2O$, %	$CO_2 + H_2$, %	α_2/α_1
0	Zn	2540	5.54	0	100	
			3.25	0.2	99.8	
			7.00	0	101	
40	Hg	2540	19.1	17.1	82.3	4.2
			11.9	26.2	73.8	3.8
			4.5	22.2	77.8	4.3
			3.1	28.0	72.0	4.4
			0.57	80.6	19.4	...
			.42	71.0	29.0	3.8
			..	75.8^a	24.2^a	...
40	Zn	2540	.62	68.1	31.9	
			.39	72.0	28.0	
			.31	72.3	27.7	
			..	75.7^a	24.3^a	
52	Zn	2540	5.53	39.7	60.3	3.9
			0.39	72.3	29.7	4.0
			..	73.3^a	26.7^a	
69.5	Hg	2540	1.33	42.6	57.4	9.3
70	Zn	2540	1.36	61.8	38.2	4.3
70	Zn	2540	0.3	71.9	28.1	
			..	72.3^a	27.7^a	
100	Hg	2540	8.0	61.8	38.2	4.2
			3.0	66.2	33.8	4.3
			1.0	68.9	31.1	4.3
			..	69.2^a	30.8^a	
100	Zn	2540	5.43	52.7	47.3	8.2
			1.66	61.0	39.0	
			1.40	70.6	29.4	
			1.40	66.4	33.6	
			..	68.2^a	31.8^a	
100	Zn	2090	13	35.2	64.8	
100			3.9	39.4	60.6	
122			5.3	42.5	57.5	
123			8.1	40.0	60.0	
100	Cd	2114	4.0	37.9	62.1	
124			20.0	38.8	61.2	
110	Al	1900	20.5	41.1	58.9	
120			22.0	42.8	57.2	
23.5	Zn	2090	27.0	0.8	99.2	
24.0			32.0	1.2	98.8	
23.6			25.4	0.0	100	
24.2			22.9	1.5	98.5	
25.0	Cd	2114	28.3	..	101	
22.6			27.5	0.8	99.2	
22.7	Al	1900	23.5	1.5	98.5	
24.4			29.6	1.0	99.0	
23.8			31.0	0.2	99.8	

[a] Signifies extrapolation to zero pressure.

---

[5] Wiig and Kistiakowsky, THIS JOURNAL, **54**, 1806 (1932).

Experimental Results.—The data on reaction products under various conditions of temperature, pressure and light source are recorded in Table II.

The quantum yield measurements are recorded in Table III.

TABLE III

QUANTUM YIELDS IN PHOTO-DECOMPOSITION OF FORMIC ACID VAPOR

Time, min.	Press. HCOOH in mm.	Temp., °C.	Press. CO + H_2 in mm. × 10^3	Quanta abs. × 10^7	Y
		1. Zn spark. λ = 2090 Å.			
15	11.8	25.0	23.4	7.57	0.98
5.86	18.8	23.0	12.68	4.67	.96
10	24.0	26.2	38.2	12.2	.99
7.95	36.5	23.0	12.25	3.99	1.06
17.5	2.5	100.5	5.2	2.76	0.65
20	3.8	101.2	2.84	2.71	.33
18	3.9	100.2	12.6	4.68	.93
14	4.4	102.0	8.54	3.38	.88
12.2	13.0	100	24.9	6.06	1.42
17.1	7.0	100	26.2	6.82	1.33
8.33	24.5	100	18.8	6.50	1.00
7.52	142	100.5	19.2	6.47	1.03
9.71	202	100.1	22.5	7.47	0.96
12.06	4.9	121.5	11.6	3.64	1.10
11.92	8.0	120	10.3	4.00	0.89
11.16	8.1	123.2	11.6	4.32	.93
7.5	20.0	124	15.5	5.09	1.06
5.60	26.8	120.2	13.0	4.68	0.96
10.5	29.0	120	20.1	7.34	.95
8.65	174	120.2	18.9	6.52	1.01
		2. Cd spark. λ = 2114 Å.			
15.2	25.2	24.4	16.5	5.94	0.96
17.6	26.8	24.6	18.7	6.16	1.05
17.0	32.1	132	15.9	6.26	.88
15.8	25.6	134	13.7	4.74	1.00
		3. Al spark. λ = 1900 Å.			
10.7	28.7	24.2	3.5	1.48	0.82
12.6	22.0	24.8	6.68	2.38	.97
8.0	26.0	128	3.24	1.02	1.10
10.5	20.5	110	5.76	1.89	1.06
		4. Zn spark. λ = 2540 Å.			
127	216	120	3.66	1.53	0.83
96	157	121.6	3.24	1.18	.95
152	182	122.2	4.47	2.72	.57
		5. HBr. λ = 2090 Å.			
	p_{HBr}		p_{H_2}		
5.35	80.9	25.0	17.6	6.11	2.00
9.8	21.8	24.0	22.8	7.84	2.02
7.83	20.9	22.8	11.5	4.07	1.95
		6. HBr. λ = 1900 Å.			
8.55	13.0	24.8	6.49	1.87	2.40
12.8	12.7	25.0	6.90	2.21	2.16
14.0	18.2	24.2	7.25	2.38	2.10

Discussion.—The results of Table II confirm the decomposition of double molecules exclusively into carbon dioxide and hydrogen throughout the entire wave length region studied. With the single molecules, the two sets of products vary in ratio with wave length and somewhat with temperature. At 40° and 2540 Å. the ratio is approximately 75.5% CO and H_2O to 24.5% CO_2 and H_2. At 100° and the same wave length it is 69 and 31%, respectively. At 2100 and 1900 Å. the ratio is 42–58 within the experimental error. The results are not dependent on the source of light used. The ratio of products varies with pressure according to equation (1). This is shown by the approximate constancy of the absorption ratio α_2/α_1 shown in the last column of Table II and to be compared with the direct measurement, 4.45, by Ramsperger and Porter.[1]

The quantum yield at 2100 and 1900 Å. is, within the experimental error, unity, independent of temperature and pressure and the same for double and single molecules. There is evidence that the yield falls at low pressures but this may be due to the difficulties of measurement. The data for 2540 Å. have a low order of accuracy due to very small light absorption, but even here the results indicate unit quantum yield.

C. Absorption Spectra.—The absorption spectra of formic acid vapor were photographed using a hydrogen discharge tube as the illuminating source and the quartz cell described in section B. At 25° and 35 mm. pressure of formic acid vapor, the absorption is continuous with a faint overlapping banded structure. Under these conditions approximately 95% of the absorption is due to double molecules. At 100° and 25 mm. pressure the absorption is strongly banded, presumably due to single molecules. Associated with these bands are numerous very narrow bands becoming more diffuse toward the far ultraviolet. The average separation between the edge of the larger bands and the first narrow band is approximately 110 cm.$^{-1}$. The character of the absorption is not changed by raising the temperature to 160° but the intensity of absorption for a given pressure increases with temperature. The spectrograms were mainly made on a Hilger E-2 instrument but, even on the largest Hilger spectrograph, there is no fine structure in any of the bands. The spectrum appears definitely to be of the predissociation type. The increased diffuseness toward the far ultraviolet probably means that the mean life of the excited single molecule is a decreasing function of the frequency of absorbed light.

The continuous absorption of the double molecule suggests that (a) the mean life of the excited state is considerably reduced by the perturbations introduced by the presence of the second acid unit in the molecule or (b) the primary process is an immediate dissociation into one normal and one excited molecule followed by dissociation of the latter. The nature of the products, exclusively $CO_2 + H_2$, would suggest a particular configuration for such an excited molecule.

The difference in the decomposition products of the single molecule obtained with 2540 Å. light from those with both 2100 and 1900 Å. may be associated with the fact that the absorption is strongly banded at the longer and continuous in the shorter wave length region.

The intensity of absorption increases continuously with the frequency. Therefore, the excitation of the molecule probably involves only one upper electronic state. This would rule out two primary reactions each from a different electronic state.

D. Experiments on Mechanism of the Primary Process.—We have employed the method of Farkas[6] and of Geib and Harteck,[7] which uses the para–ortho hydrogen conversion as a quantitative test for hydrogen atoms, to ascertain whether hydrogen atoms are formed in the primary process of photo-decomposition of formic acid. The acid was decomposed by light from a zinc spark in the presence of para-rich hydrogen and the amount of conversion to the equilibrium mixture determined by the thermal conductivity method of Bonhoeffer and Harteck.[8] The hydrogen used was approximately 43.5% para, prepared over charcoal at liquid air temperatures. Carbon dioxide, residual formic acid and water were removed from the product gases by liquid air. Carbon monoxide was removed by circulation of the gas for one hour over iodine pentoxide heated to 110°, the resulting iodine and carbon dioxide being frozen out in liquid air. Blank tests revealed that no detectable conversion of para hydrogen occurs with such treatment in five hours. The experimental results are shown in Table IV.

TABLE IV

Press. HCOOH in mm.	Press. 1:1 H_2 in mm.	HCOOH decomp. in mm.	Temp., °C.	Time, min.	x_0	x	(H) in mm. $\times 10^7$	k_1' $\times 10^6$
34.7	165.6	12.7	132.4	77	0.426	0.348	4.4	0.31
38.0	163.5	8.5	130.0	73	.431	.351	4.2	.38
23.8	128.0	16.3	110.0	45	.416	.359	7.8	.33
22.0	482.3	5.3	110.4	44	.433	.393	4.6	1.01
25.0	568.2	18.4	110.2	32	.428	.394	6.4	0.49
22.4	99.0	16.2	110.0	25	.409	.350	18.0	.66
21.0	138.9	8.2	26.9	85	.426	.406	19.0	10.6
19.8	190.8	10.3	26.9	65	.425	.412	13.0	3.7
28.7	239.9	33.4	26.0	56	.416	.401	22.0	3.4
37.3	144.2	25.6	30.2	77	.411	.382	24.5	5.6

We wish at this point to express our appreciation to Dr. John Turkevich for assistance rendered in the ortho–para hydrogen determinations.

The rate of conversion of para to ortho hydrogen by atomic hydrogen may be expressed by the equation

$$-\frac{d([H_2]_p)}{dt} = k_1[H][H_2]x - k_2(1 - x)[H][H_2]$$

where x is the fraction of para hydrogen present, k_1 and k_2 the rate constants of the forward and backward reactions. At equilibrium $x = {}^1/_4$ and hence $3k_2 = k_1$. Introducing this value for k_2 and integrating we obtain

$$\log \frac{x_0 - 1/4}{x - 1/4} = 4/3\, k_1[H]t$$

where x_0 and x are the fractions of para hydrogen initially and at time t.

Geib and Harteck[7] have given values for the collision yield at 10, 57 and 100° and an activation energy of 7250 calories. From these data we deduce the following values of k_1 in units of mm.$^{-1}$, sec.$^{-1}$; at 132°, 2.82×10^2; 130°, 2.72×10^2; 110°, 1.72×10^2; 27°, 14.6.

If we assume that the primary photo process involves a dissociation into radicals

$$HCOOH + h\nu = H + COOH\ (k_1')$$

followed by an immediate decomposition of the COOH radical into $CO_2 + H$ and a termolecular combination of hydrogen atoms on the hydrogen molecules present (k_2') in these experiments, it can readily be shown that the stationary hydrogen atom concentration [H] is given by an expression

$$[H] = \sqrt{k_1' I_{abs.}/k_2' P}$$

If we express $I_{abs.}$ in terms of mm. of formic acid decomposed per second, P the total pressure in mm. and k_2' in mm.$^{-2}$ sec.$^{-1}$, then k_1' is the fraction of the total number of primary processes which result in a hydrogen atom split. We have em-

---

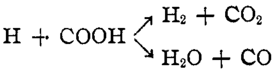
(6) Farkas, *Z. physik. Chem.*, **10B**, 419 (1930).

(7) Geib and Harteck, *ibid.*, Bodenstein Festband, 849 (1931).

(8) Bonhoeffer and Harteck, *ibid.*, **4B**, 113 (1929).

ployed the data of Steiner and Wicke[9] for k_2'. Later data of Amdur and Robinson[10] would not alter our conclusions materially. At 27° the value is 28.6, from which we deduce a value of 21.45 at 130°. With these data we calculate the quantities for k_1' shown in the last column of Table IV. The approximate constancy of k_1' over a five-fold range in pressure and a six-fold variation in $I_{\text{abs.}}$ is a measure of the validity of our assumed mechanism of hydrogen atom recombination.

It is evident from the magnitude of k_1' that only about one to ten primary processes per million give rise to a hydrogen atom. If we assume that reaction of hydrogen atoms and COOH radical is the mechanism of decomposition



$$H + COOH \begin{cases} \nearrow H_2 + CO_2 \\ \searrow H_2O + CO \end{cases}$$

a reaction of these *on every collision*, would only raise k_1' by a factor of 10^{-3} and would still leave the radical split a very minor fraction of the total decomposition. This result is an experimental demonstration of the reservation made by Franck and Rabinowitsch[11] concerning gaseous photochemical decomposition processes proceeding through the intermediary of atoms and free radicals. They specifically excepted from their generalization the case of a possible dissociation into saturated molecules, and cited the organic acids RCOOH dissociating into $RH + CO_2$ as examples. In the special case of formic acid with still another mode of decomposition to the saturated molecules $H_2O + CO$ the exception also holds. These two modes of decomposition each to give two saturated molecules represent the great majority of the secondary processes succeeding the primary absorption of light. The distribution between the two alternatives is determined exclusively in favor of $CO_2 + H_2$ with the double molecules; in the single molecules at the long wave length limit of the absorption the majority decompose in the other way, to $CO + H_2O$. With increase of temperature or with shorter wave lengths the split between the two alternatives is displaced toward $CO_2 + H_2$, the effect of decreasing wave length being much more pronounced than increase of temperature. In every case light absorption is always followed by decomposition.

Summary

1. The products of photo-decomposition of single formic acid molecules are carbon monoxide and water and carbon dioxide and hydrogen. The two former predominate at longer wave lengths of illumination. The ratio is displaced toward the latter products with increase of temperature and increase of light frequency.

2. The products of photo-decomposition of double formic acid molecules are exclusively carbon dioxide and hydrogen in the whole wave length region from 1900 to 2540 Å.

3. The decompositions of the two species of molecule are independent and the quantum yield is unity for each species, independent of temperature and pressure over considerable ranges.

4. The ultraviolet absorption spectrum of the double molecule is continuous; that of the single molecule is banded and of the predissociation type.

5. The primary process of absorption leads to decomposition to form saturated molecules, with minimal formation of hydrogen atoms and radicals.

PRINCETON, N. J.

RECEIVED JULY 28, 1934

---

[9] Steiner and Wicke, *Z. physik. Chem.*, Bodenstein Festband, 817 (1931).

[10] Amdur and Robinson, THIS JOURNAL, **55**, 1395, 2615 (1933).

[11] Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).