[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Studies in the Mechanism of Decomposition. II. Note on the Photolysis of Formic Acid

BY MILTON BURTON

Using the para–ortho hydrogen conversion method of Farkas[1] and of Geib and Harteck,[2] Gorin and H. S. Taylor[3] adduced good evidence that no atomic hydrogen is produced during the photolysis of formic acid and that the decomposition probably proceeds by a rearrangement of bonds to yield stable molecules in one primary act by one of the two reactions

$$HCOOH + h\nu \longrightarrow H_2O + CO \qquad (1)$$

$$HCOOH + h\nu \longrightarrow H_2 + CO_2 \qquad (2)$$ [4]

Inasmuch as evidence has been presented[5] that hydrogen atom is formed during the photolysis of acetic acid, the question naturally arose as to whether Gorin and Taylor's failure to observe similar results for formic acid might not be a consequence of the method they employed. Accordingly, the tests described below were undertaken to discover whether the mirror method might detect hydrogen atoms in the photolysis of formic acid.

Experimental

The apparatus and methods used were similar to those described for acetic acid.[5] A sample of Kahlbaum Formic Acid 95% was dried over Drierite for three days, introduced into the carefully evacuated system and degassed as already described for acetic acid. In the runs the pressure of formic acid was fixed at about 2.4 mm. at the sloping manometer before the constricted region of the reaction system. Only antimony mirrors were used in the reaction tube. With the capillary mercury arc previously described[5] located 22.8 cm. from the beginning of the reaction tube and 1 cm. from it, antimony mirrors were deposited in the usual manner at about 9 cm. from the irradiated zone.

Tests for Atomic Hydrogen.—In none of the experiments with illuminated formic acid was removal of the antimony mirrors ever observed. In one case, a typical run failed to affect a very light antimony mirror, which would not have lasted four minutes with acetic acid under the same conditions, even though continued for seventy-eight minutes. The system was checked with fresh acetic acid according to the methods previously described and the mirrors were found to possess their normal sensitivity.

There is, of course, the possibility that the energy of activation of secondary reactions between H and HCOOH may be so low that reaction takes place on the first collision or, at most, after a very few collisions and that consequently the hydrogen atoms, though formed, never reach the mirror. This possibility was checked by making a run with a mixture containing approximately 4 parts of acetic acid to about 1 of formic acid. It being already known that photolyzed acetic acid yields hydrogen atoms, such a run should afford a direct test of a possible very fast reaction between H and HCOOH. With the pressure of the mixed vapor adjusted at about 2.4 mm. at the sloping manometer and the other conditions being as already described, it was found that a mirror which would not last in pure acetic acid vapor for more than about four minutes now took about sixteen minutes to disappear. It may be concluded from this test either that formic acid acts like acetaldehyde[6] and reduces normal mirror activity or that there is a rather rapid reaction between H and HCOOH, faster than that between H and CH_3COOH but not fast enough to account for a failure to observe hydrogen atoms during the photolysis of formic acid if there formed.

In order to check the first alternative a formic acid run was made in which the antimony mirror was heated with live steam. Although continued for fifty-two minutes, not the slightest effect was observed on a very light antimony mirror such as used in this group of experiments. Inasmuch as the mixed run with acetic acid had already demonstrated that formic acid did not have a completely deadening effect on the antimony mirror, it may be concluded from this experiment that the failure to observe mirror removal was not due to a cause similar to that reported for acetaldehyde; *i. e.*, the mirrors were not being made inactive by a condensed layer of formic acid.

In a final experiment with formic acid, the arc was brought up to within 0.7 cm. of the reaction tube and a very light antimony mirror deposited 1.9 cm. from the irradiated zone. Although the run was continued for forty-seven minutes, no indication of sharpening of the mirror (a phenomenon always occurring long before removal) was observed.

The absorption spectra of formic acid and of acetic acid are very similar,[7] the extinction coefficients throughout the continua being almost the same, except that the spectrum of formic acid is displaced slightly toward the long wave side. Inasmuch as decomposition of acetic acid has been detected under the conditions of these experiments and Gorin and Taylor have already demonstrated the photolysis of formic acid at wave lengths which the arc used has been shown to cover,[5] it appears reasonable to assume that decomposition of the formic acid also occurred. Consequently, the evidence recited above appears to indi-

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[1] Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

[2] Geib and Harteck, *ibid.*, Bodenstein-Festband, 849 (1931).

[3] Gorin and Taylor, THIS JOURNAL, **56**, 2042 (1934).

[4] These are the over-all reactions. The mechanism was not suggested but the intimation was that it would be quite different, since double molecules are mainly involved in reaction 2.

[5] Burton, THIS JOURNAL, **58**, 1645 (1936).

[6] Pearson, *J. Chem. Soc.*, 1718 (1934); Pearson and Purcell, *ibid.*, 1151 (1935).

[7] Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

cate that no hydrogen atoms are formed during the photolysis of formic acid.

The stability of HCO.—The results of Blacet and Roof[8] on the photolysis of acetaldehyde indicate that the HCO radical is rather stable. On the other hand, although the data used by Rice and Herzfeld[9] in considering the chain mechanism involved in the pyrolysis of that compound would indicate a fair stability of HCO at room temperature, Mecke,[10] in discussing the photolysis of formaldehyde, favored the idea that HCO is very unstable and requires only about 4 kcal. to dissociate it further.

Using the guard mirror method previously described[5,11] and employing the precautions indicated to be necessary by the work of Pearson and Purcell,[6] it was found in a preliminary experiment with acetaldehyde, purified[12] and evacuated (using liquid air) in the regular manner, that the light lead mirror, before the lead guard mirror, was removed in five minutes while the light antimony mirror, after the guard, was not in the slightest degree affected after seventy-one minutes.

Inasmuch as CH_3 was formed, HCO must have been formed and the inference logically follows that HCO must be very stable at room temperatures since, had it decomposed, atomic hydrogen would have been formed and would have removed the antimony mirror.

Discussion

Terenin[13] has reported the emission spectrum of hydroxyl during the photolysis of formic acid. If we assume a possible mechanism to account for this production as follows

$$HCOOH + h\nu \longrightarrow HCOOH^* \qquad (3)$$

$$HCOOH^* \longrightarrow HCO + OH \qquad (4)$$

it is evident that no H atom need be observed, since, as has been shown, HCO does not appear to decompose readily. Although OH had been similarly discovered in the photolysis of acetic acid, its formation in a primary step had been excluded because of the known instability of CH_3CO.[14] In the case of formic acid the strength of the C–H bond may be presumed to be greater than that of the C–C bond in acetic acid.[15] It consequently seems that the C–O bond may be much weaker in formic acid than in acetic acid. Since the evidence of absorption spectra indicates that absorption in both compounds is in the COOH group, it may well be possible that the C–O bond is weaker than the O–H bond in formic acid and that the decomposition takes place at the weaker bond.

The para–ortho hydrogen conversion should be as sensitive to a free radical such as OH as to free H.[16] However, if it be ignored for the moment that the results of Gorin and Taylor, contrary to the findings of Terenin, exclude the possibility of any considerable formation of OH, it would still be difficult to write a completely satisfactory free radical reaction mechanism to fit the known data (except by a process of strictly *ad hoc* reasoning) because of the complication introduced by the predominance of double formic acid molecules at pressures greater than 10 mm. and temperatures below 30°.[17] It would be hard to explain why double molecules decompose exclusively by reaction 2. It consequently appears advisable in view of the present state of knowledge of this reaction not to attempt the hypothesis of a mechanism beyond reactions 3 and 4.

The antimony mirror indicates, in agreement with the results of Gorin and Taylor, that no hydrogen atoms are formed in the photolysis of formic acid at room temperatures. This result, it has been shown, is not inconsistent with the findings of Terenin that OH is formed during such photolysis. However, it appears that it may be difficult to reconcile Terenin's results with those of Gorin and Taylor. In view of the evidence, it still appears advisable to consider the photolysis of formic acid as being predominantly a decomposition into stable molecules in one primary act[18] for very little OH has to be produced to be detectable by its emission spectrum.[19]

Acknowledgment.—The author wishes to express his appreciation to Professor H. Austin Taylor for his advice and suggestions.

Summary

1. No hydrogen atoms are detectable by the antimony mirror method during the photolysis of formic acid. This agrees with the findings of Gorin and Taylor.

2. Evidence presented indicates that a reaction takes place between H and HCOOH with a fairly low energy of activation.

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[8] Blacet and Roof, THIS JOURNAL, **58**, 278 (1936).

[9] Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

[10] Mecke, *Nature*, **125**, 526 (1930).

[11] Burton, THIS JOURNAL, **58**, 692 (1936).

[12] The vapor pressure at 0° was 336.7 ± 0.8 mm. which checks with the value of 337 mm. given by Emeleus [*J. Chem. Soc.*, 1733 (1929)].

[13] Terenin, *Acta Physicochim. U. R. S. S.*, **3**, 181 (1935).

[14] Norrish, *ibid.*, **3**, 171 (1935)

[15] For a full discussion of bond strengths see Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, 1935, Chap. VI.

[16] *Cf.* L. Farkas and Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933); *Trans. Faraday Soc.*, **30**, 331 (1934); A. Farkas, "Ortho-Hydrogen, Para-Hydrogen, Heavy Hydrogen," Cambridge University Press, 1935, p. 102; W. West, THIS JOURNAL, **57**, 1931 (1935).

[17] *Cf.* ref. 10; also Ramsperger and Porter, THIS JOURNAL, **48**, 1267 (1926); Coolidge, *ibid.*, **50**, 2166 (1928).

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

[19] Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).

3. A mechanism is suggested for the formation of OH during the photolysis of formic acid. This mechanism is consistent with the mechanism previously suggested for acetic acid.

4. A preliminary experiment with acetaldehyde showed HCO to be a stable radical at room temperature.

5. In view of the difficulty in reconciling the results of Gorin and Taylor with those of Terenin, it appears probable that the major portion of the photolysis of formic acid takes place by decomposition into stable molecules in one primary act.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MONTANA STATE UNIVERSITY]

Cyclohexyltrichloromethylcarbinol

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This compound was prepared by the reaction of chloral and cyclohexylmagnesium bromide. The most satisfactory results were obtained when this was carried out as an "inverse Grignard" reaction.

The Grignard reagent was prepared by adding 82 g. of monobromocyclohexane in 60 cc. of ether to 14 g. of magnesium ribbon and a crystal of iodine in 70 cc. of ether. The reaction was completed after three hours of stirring and gentle heating. The resultant solution was decanted from any unchanged magnesium and added with stirring over a two-hour period to 74 g. of freshly distilled chloral in 150 cc. of ether. The product was decomposed with 30% sulfuric acid and the ether washed in turn with water, sodium bicarbonate solution, sodium bisulfite solution and water. It was dehydrated over anhydrous sodium sulfate, the ether removed by distillation and the alcohol distilled in vacuum. A yield of 35 g. of an oily liquid boiling at 119 to 121° at 15 mm. was obtained; d^{20}_{20} 1.2839, n_{25} 1.4820. *Anal.* Calcd. for $C_8H_{13}OCl_3$: Cl, 45.95. Found: Cl, 45.99.

This carbinol darkens on standing. It is insoluble in water but soluble in ether, ethyl alcohol, methyl alcohol, acetone, benzene, chloroform and carbon tetrachloride.

Preparation of the Esters

The acetate and propionate were prepared by refluxing the carbinol for one and one-half hours at 135° with the corresponding acid chloride. The same method was used to prepare the butyrate but butyric anhydride was found to give more satisfactory results than butyryl chloride. The benzoate was prepared by treatment with benzoyl chloride according to the usual procedure of the Schotten–Baumann reaction.

ESTERS OF CYCLOHEXYLTRICHLOROMETHYLCARBINOL

		Formula	Analysis for Cl, % Calcd.	Analysis for Cl, % Found
1	Acetate	$C_{10}H_{15}O_2Cl_3$	38.89	39.08
2	Propionate	$C_{11}H_{17}O_2Cl_3$	36.97	37.14
3	Butyrate	$C_{12}H_{19}O_2Cl_3$	35.44	35.28
4	Benzoate	$C_{15}H_{17}O_2Cl_3$	31.71	31.56

	B. p., °C.	Mm.	d^{20}_{20}	n_{25}
1	173	680	1.3612	1.4945
2	188	681.6	1.2119	1.4989
3	185	682.6	1.1872	1.4995
4	210	683.3	1.2893	1.5259

The average yields of these esters was 85%. They are all insoluble in water but soluble in ether, ethyl alcohol, methyl alcohol, acetone, benzene, chloroform and carbon tetrachloride.

Summary

Cyclohexyltrichloromethylcarbinol as well as its acetic, propionic, butyric and benzoic esters have been prepared and studied.

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