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

# Studies in the Mechanism of Decomposition. III. The Vapor Phase Photolysis of Propionic Acid

BY H. HENKIN AND MILTON BURTON[1]

It has been shown by E. Gorin and H. S. Taylor[2] and verified by Burton,[3] that no hydrogen atoms are formed in the photolysis of formic acid and that the decomposition probably proceeds with the formation of ultimate molecules in one primary act. L. Farkas and Wansbrough-Jones[4] had concluded on the basis of analysis of the products and determination of the quantum yield that acetic acid likewise decomposes into stable molecules in the initial step but it has been shown[5] that in that case also part of the decomposition proceeds via the intermediary of free hydrogen atoms and radicals.

There have been no studies of the photolysis of propionic acid vapor but Pierce and Morey[6] and Farkas and Wansbrough-Jones[4] have studied the photodecomposition of its aqueous solutions. The former report that the chief products of the photolysis are ethane and carbon dioxide, from the reaction

$$C_2H_5COOH + h\nu \longrightarrow C_2H_6 + CO_2 \qquad (1)$$

whereas the latter state that the reaction

$$C_2H_5COOH(H_2O) + h\nu \longrightarrow C_2H_5OH + HCOOH \qquad (2)$$

takes place to about 0.6 times the extent of reaction 1. As in the other cases, the decomposition has been presumed to proceed by rearrangement of a stable constellation of groups into stable constellations of ultimate molecules.

In this paper evidence is presented which indicates that in the photolysis of propionic acid vapor, as in that of acetic acid, hydrogen atoms are produced. The relative number of hydrogen atoms produced per einstein absorbed appears to be greater in the case of propionic acid than in the case of acetic acid.

## Experimental

The general technique employed in this investigation was to pass the vapor of the substance under investigation through a quartz tube at a known rate and pressure. The streaming vapor was exposed, during runs, to the light of a mercury arc of fairly steady intensity and thereafter passed over the surface of a prepared standard mirror according to the method developed by Paneth and by Rice and his co-workers.[7] It has been shown that lead mirrors are removed by free alkyl radicals but not by hydrogen atoms whereas antimony mirrors are sensitive to both. Unless otherwise indicated, the apparatus and technique employed were similar to those described by Burton in the study of acetic acid.[5]

**Light Source.**—A constricted quartz mercury arc similar to the one previously described[5] was operated at 2.4 amperes. The capillary portion of the arc was exactly 2 mm. in internal diameter. It has been found that, in order to operate at the higher amperages (4–5 amperes) previously mentioned, the internal diameter of the capillary must be about 2.7 mm.

**Chemicals.**—The acetic acid used was purified and introduced into the system, as previously described. A sample of Kahlbaum propionic acid was dried over Drierite for two days and then fractionally distilled several times, the final distillate coming over at a temperature (corrected) of 140.5–140.8°. It was introduced into the carefully evacuated system in the same manner as the acetic acid. Each liquid was thoroughly degassed as already described.

**Apparatus and Technique.**—There has been no substantial change in the practice of the previous paper. Lubriseal grease was used on all stopcocks and joints. It may be remarked that the propionic acid, especially, attacked the grease fairly readily and the stopcock on the propionic acid reservoir had to be regreased repeatedly. The length of the constricted portion of the tubing, including the quartz reaction tube and joints, was fixed at 128 cm. The average internal diameter of the quartz reaction tube was 0.549 cm. The mercury manometer[8] used had a slope ratio of 25:1 and permitted readings accurate to 0.01 mm. All pressures given are at this manometer, *i. e.*, they are the pressures in the wide part of the system before admission of the gas into the reaction line.

Throughout all the experiments, the far side of the mercury arc was kept 62.8 cm. from the beginning of the constricted portion of the reaction system and 0.75 cm. in front of the quartz tube. Both arc and quartz reaction tube were cooled thoroughly and, except for the portion deliberately exposed to the arc during runs, the reaction tube and the lead or antimony mirrors deposited in it were shielded from the light source by water-cooled copper cylinders. In certain experiments, noted later, the mirrors were heated with steam. In those cases the glass steam jacket prevented the access of the photoactive ultraviolet light to the mirrors.

---

[1] Present address: Department of Chemistry, University of California, Berkeley, Calif.

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

[3] Burton, *ibid.*, **58**, 1655 (1936).

[4] Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).

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

[6] Pierce and Morey, *ibid.*, **54**, 467 (1932).

[7] For a thorough discussion of the mirror method *cf.* F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935.

[8] Burton, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 335 (1937).

**Part I. Atomic Hydrogen in the Photolysis of Propionic Acid.**—In order to determine whether any alkyl radicals were produced during the photolysis of propionic acid very faint lead mirrors were deposited within 5–7 cm. of the irradiated zone, but no sign of mirror removal (nor of characteristic sharpening of the mirror) was noted at the end of fifty-five to sixty minutes after exposure of the flowing propionic acid vapor. It will be shown that heavier antimony mirrors similarly located are removed in approximately thirty minutes. It already has been shown[5] that when lead and antimony mirrors of visually equal weight are similarly employed, methyl radicals attack the former about three times as rapidly as the latter. It is therefore extremely improbable that any alkyl radicals are present during the photolysis of propionic acid. For a reason which will appear later, similar tests were conducted with the lead mirror (at a distance of about 8 cm. from the irradiated zone) surrounded by a steam jacket at 100°. In these cases the mirrors were not removed in one hundred and ten to one hundred and twenty minutes. In one case there was a slight sharpening of the mirror. If any alkyl radicals were formed under these conditions, the amount is practically undetectable by this method.

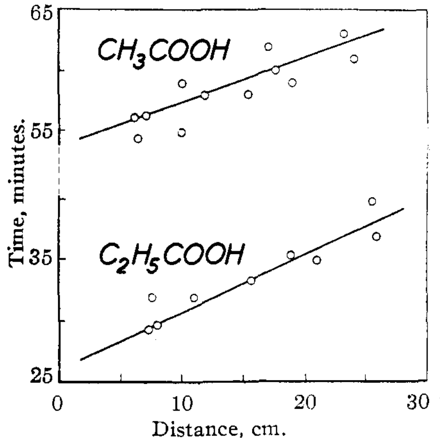

Fig. 1.—Variation of time required for mirror removal with distance from irradiated zone.

As has already been mentioned, the results obtained with standard antimony mirrors were quite different. As may be seen from Fig. 1, such mirrors were readily removed at distances up to 26 cm. from the irradiated zone when the propionic acid was illuminated; in blank runs without irradiation no effect was observed. It may be inferred from this result that atomic hydrogen is formed in the primary step according to some such reaction as

$$C_2H_5COOH + h\nu \longrightarrow C_2H_5COO + H \quad (3)$$

The products observed in the photodecomposition (in aqueous solution) make it unlikely that the atomic hydrogen produced by the photolysis of the vapor comes from the alkyl group, for in that event a greater complexity of products would be expected.

The reaction

$$C_2H_5COOH + h\nu \longrightarrow C_2H_5CO + OH \quad (4)$$

probably does not occur for, if it did, the free OH radicals might be expected to inhibit the removal of the antimony mirrors. On the other hand, if the free OH radicals do not display this effect, the free $C_2H_5CO$ radical would be expected to decompose readily at 100°,[9] in part, at least, according to the reaction

$$C_2H_5CO \longrightarrow C_2H_5 + CO \quad (5)$$

Since the lead mirror is not affected, it may be concluded that reaction (4) and the subsequent reaction (5) do not occur.

**Part II. Effect of Distance of Mirror from the Irradiated Zone.**—It has been shown in the case of acetic acid[5] that the shape of the curve obtained by plotting time of mirror removal against distance of the mirror from the irradiated zone, with constant streaming velocity, is quite characteristic of the nature of the radical involved. When free hydrogen atoms are the effective instruments of mirror removal the curve is a straight line almost parallel to the distance axis. The results obtained in a series of experiments conducted at a pressure of ~0.242 cm. at the manometer are shown in Fig. 1. It is seen that the curve is characteristic of hydrogen atoms. The somewhat greater slope than that obtained in the previous work[5] on the photolysis of acetic acid is due in part to two causes, namely, a lower activation energy for the subsequent reactions involving atomic hydrogen, *e. g.*

$$RCOOH + H \longrightarrow RH + COOH \quad (6)$$

and the somewhat slower streaming velocity in this work, which affords a greater opportunity for reactions such as (6).

---

[9] Burton, *J. Phys. Chem.*, **41**, 322 (1937); THIS JOURNAL, **58**, 1655 (1936); *ibid.*, **60**, 212 (1938), has shown that the free HCO radical is stable up to temperatures of 100°. Spence and Wild, *J. Chem. Soc.*, 352 (1937), have shown that the free $CH_3CO$ radical is stable at room temperature but not at 60°. By analogy free $C_2H_5CO$ should be even less stable.

In Fig. 2 there is given a calibration curve indicating the time required to transfer a gram molecule of propionic acid at various pressures. The calculation of the streaming velocity, $V$, at any pressure from such a curve requires knowledge of the vapor density, which does not seem to have been studied in the case of propionic acid. At 25° acetic acid is highly associated even at 3 mm. pressure. If it be assumed that in this respect propionic acid behaves similarly to acetic acid,[10] extrapolations may be made from the data given by MacDougall[11] for the density of acetic acid vapor; calculations from Fig. 2 then show that, when the pressure at the entrance to the constricted region is 0.242 cm., $V$ is $9.83 \times 10^2$ cm. per sec. If it be assumed that unlike the acetic acid the propionic acid is completely associated into the dimer at room temperature and 0.242 cm., the calculated value of $V$ then appears to be only $8.06 \times 10^2$ cm. per sec. Although the data pictured in Fig. 2 were determined directly, it is evident that the streaming velocity in these experiments is merely an estimated quantity.

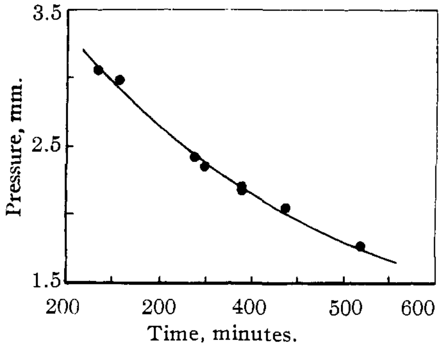

Fig. 2.—Time required for 1 mole of propionic acid to flow through reaction system at various pressures.

A similar series of experiments was performed with acetic acid using a pressure of ~0.305 cm. corresponding to a streaming velocity of $7.98 \times 10^2$ cm. per sec., the latter figure being calculated from the calibration curve of Fig. 3 using MacDougall's data for the vapor density. The results are shown in Fig. 1, where they may be contrasted with the propionic acid results.

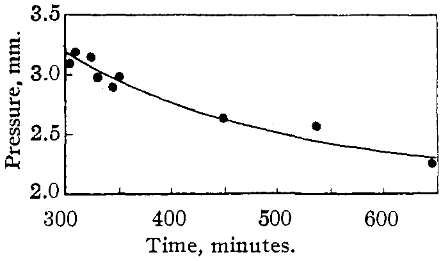

Fig. 3.—Time required for 1 mole of acetic acid to pass through reaction system at various pressures.

Comparison of Figs. 2 and 3 also shows an interesting contrast. The transport of propionic acid is considerably more rapid than that of acetic acid at the same pressure and temperature. It is such a result which suggests the possibility that propionic acid may be completely associated into the dimer under the conditions of the experiments and it is for this reason that in the next paragraph and in Table I calculations are made for that substance on the basis of two values of $V$, namely, $9.83 \times 10^2$ and $8.06 \times 10^2$ cm. per sec., the latter corresponding to complete association.

The results so far indicated may be used to calculate the activation energy of the disappearance of atomic hydrogen in the two cases. The method used is the same as that described in the earlier paper, to which the reader is referred for an explanation of the symbols. In that paper the dimerization of the acetic acid was not taken into account in calculation of the streaming velocity. Such a correction changes the results slightly. In Table I there is indicated an outline of the calculation of the energy of activation of disappearance of H atom in the several cases (assuming a steric factor of unity). Columns A and B show

TABLE I

CALCULATION OF ACTIVATION ENERGY OF DISAPPEARANCE OF ATOMIC HYDROGEN

| | Propionic acid | | Acetic acid | |
|---|---|---|---|---|
| Substance | A | B | C This paper | D Burton |
| $P$, cm. | 0.242 | 0.242 | 0.305 | 0.23 |
| Length of system, cm. | 128 | 128 | 128 | 88 |
| Diam., cm. | 0.549 | 0.549 | 0.549 | .5 |
| $V \times 10^2$ cm./sec. | 9.83 | 8.06 | 7.98 | 18.3 |
| $a \times 10^3$ | 1.89 | 1.89 | 2.38 | 2.61 |
| $X_1$, cm. | 62.8 | 62.8 | 62.8 | 22.8 |
| $X_2$, cm. | 82.8 | 82.8 | 82.8 | 52.8 |
| $t \times 10^2$, sec. | 0.876 | 1.057 | 1.19 | 0.94 |
| $A \times (10^{-5}$ or $10^{-6})$ | 1.203 | 1.467 | 2.06 | 1.63 |
| $k$ | 0.2655 | 0.2655 | 0.118 | 0.13 |
| $E$, kcal. | 7.7–9.1 | 7.8–9.2 | 8.5–9.9 | 8.3–9.7 |

---

[10] Prof. J. H. Hildebrand suggested to one of us (M.B.) that this may be a reasonable assumption since the strengths of the hydrogen bonds existent in the dimer probably are not affected markedly by change in the length of the aliphatic radical connected to the COOH group. Such a conclusion is consonant with the results of Broughton, *Trans. Faraday Soc.*, **30**, 367 (1934), who studied the association in cyclohexane solution. The procedure here used is justified *at this point* by the fact that a considerable error in this estimate has but a slight effect on the subsequently determined value for the energy of activation.

[11] MacDougall, THIS JOURNAL, **58**, 2585 (1936).

the calculations on the respective assumptions that propionic acid behaves precisely like acetic acid and that it is completely dimerized. Columns C and D show the calculations for acetic acid based, respectively, on the data of this paper and on those of the previous paper.

It may seem from the table that the activation energy in the case of acetic acid is 8.5–9.9 kcal. in fair agreement with the figure of 8.3–9.7 based on the previous work. This activation energy is slightly higher than that of 7.7–9.2 kcal. calculated in the case of propionic acid. The spread of the calculations arises from the necessity of making assumptions as to the number of collisions suffered by a hydrogen atom under the conditions of the experiment, as well as from the question of vapor density in the case of propionic acid.

**Part II. The Effect of Pressure on the Rate of Mirror Disappearance.**—Tests were also conducted over a range of pressures both in the case of propionic acid and in that of acetic acid, with the antimony mirror at a fixed distance of ~ 24.0 cm. from the irradiated zone and the edge of the irradiated zone, as before, at 62.8 cm. from the beginning of the constricted portion of the system. The results for both acids are pictured in Fig. 4. The two cases are not directly comparable, for the pressure at the manometer is but an indirect indication of the number of molecules, dimeric molecules being counted as two, in the irradiated zone.

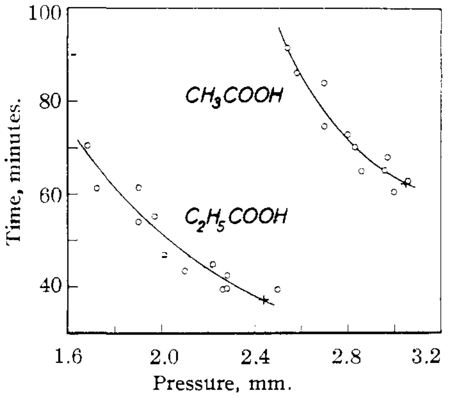

Fig. 4.—Variation of time required for mirror removal with pressure. In each case, the point designated + is taken from Fig. 1.

It was the purpose of this series of experiments to obtain information as to the relative amounts of atomic hydrogen production per einstein absorbed in the two cases. Since it was not practical to measure the amount of light absorbed, an estimate must be made. It has been shown by Ley and Arends[12] that acetic and butyric acids have nearly equal extinction coefficients (*i. e.*, within ~10%) over the range of the continuum above 1849 Å. Although propionic acid has not been studied, it may be presumed that its extinction coefficient is similar to that of acetic acid. Therefore, the condition for equal absorption of light by the two acids is simply the condition of equal numbers of molecules in the irradiated zone in the two cases. Obviously, the results of the calculations depend on the assumed degree of association of propionic acid.

If the assumption is correct that under like conditions (at 25°) acetic and propionic acids are equally associated, then the results in Fig. 4 can be compared only at equal pressures. Propionic acid at an entering pressure of 2.5 mm. removes an antimony mirror in 36.0 minutes, while 95.6 min. are required for acetic acid at the same entering pressure. Thus it appears that in propionic acid at that pressure 95.6/36.0 or ~2.7 times as many hydrogen atoms are present 24.0 cm. from the irradiated zone as in acetic acid. Since it appears from the values for the activation energy that hydrogen atoms disappear more rapidly in propionic acid than in acetic acid, this value of ~2.7 is a lower limit for the ratio at the irradiated zone. Calculations may be carried out which are somewhat the inverse of those shown in Table I. In this way it is found that the ratio of hydrogen atoms produced at the irradiated zone (assuming that propionic acid and acetic acid are similarly dimerized) is ~3.3.

On the other hand, since Figs. 2 and 3 indicate that the vapor of propionic acid is far less viscous than that of acetic acid, it is possible that the propionic acid is entirely associated into dimeric molecules. Acetic acid is approximately 20% dissociated in the range of pressure studied. Assuming complete dimerization of the propionic acid, it is evident that equal volumes of the two gases contain the same number of single molecules (counting dimers twice) when the pressure of acetic acid is roughly 1.2 times that of propionic acid. Comparison of rates of mirror removal at such corresponding pressures is made in Table II. In that table, $P$ represents the pressure in cm. at the manometer, $t_{Ac}$ the time in minutes required for removal of an antimony mirror by acetic acid

---

[12] Ley and Arends, *Z. physik. Chem.*, **B4**, 234 (1929).

vapor, $t_{Pr}$ the time for propionic acid, and $R$ the ratio of hydrogen atom production (propionic acid: acetic acid) in the irradiated zone, based in this case on the assumption that propionic acid is completely dimerized and calculated by a procedure inverse to that outlined in Table I.

TABLE II

COMPARISON OF TIMES OF MIRROR REMOVAL AT ROUGHLY "CORRESPONDING" PRESSURES

| Acetic acid | | Propionic acid | | | |
|---|---|---|---|---|---|
| $P$ | $t_{Ac}$ | $P$ | $t_{Pr}$ | $t_{Ac}/t_{Pr}$ | $R$ |
| 0.30 | 63.8 | 0.25 | 36.0 | 1.77 | 2.3 |
| .29 | 67.4 | .242 | 37.5 | 1.80 | 2.3 |
| .28 | 71.7 | .233 | 39.8 | 1.80 | 2.4 |
| .27 | 77.9 | .225 | 42.2 | 1.85 | 2.4 |
| .26 | 85.5 | .217 | 44.7 | 1.91 | 2.5 |
| .25 | 95.6 | .209 | 47.8 | 2.00 | 2.6 |

It appears from these calculations, regardless of the assumptions made as to the degree of association of propionic acid, that the amount of atomic hydrogen production per einstein absorbed is at least 2.3 times as great in the case of propionic acid as in that of acetic acid.

**Part IV. Test for Free Methyl in Acetic Acid Photolysis.**—In the previous paper it was assumed (in accordance with the then current views) that the reaction

$$CH_3CO \longrightarrow CH_3 + CO \qquad (7)$$

goes instantaneously at room temperature. Because Spence and Wild[13] have since shown $CH_3CO$ to be stable at room temperature but unstable at 60°, runs like those described above were made with acetic acid using lead mirrors heated in a steam jacket at 100°. The mirrors were unaffected in one hundred and ten to one hundred and twenty minutes even when located within 8 cm. of the irradiated zone. It consequently appears that the earlier conclusion, that the reaction

$$CH_3COOH + h\nu \longrightarrow CH_3CO + OH \qquad (8)$$

does not occur to any appreciable extent, is correct.

## Discussion

The purpose of this investigation was to discover what, if any, effect the length of the carbon chain has on the primary step in the decomposition of the aliphatic acids. The results of Part III definitely show that the rupture process

$$RCOOH + h\nu \longrightarrow RCOO + H \qquad (9)$$

is increased more than 100% per einstein absorbed as we pass from acetic to propionic acid, while in the case of formic acid the reaction appears to go exclusively by a rearrangement process.[2,3] If the primary step be presumed to proceed with a quantum yield of unity, it must be concluded that in the case of acetic acid, at any rate, the decomposition must proceed in part via a rearrangement mechanism to give ultimate molecules in one primary act as well as by the rupture mechanism. It is not possible with the data at hand to state to what relative extents these two processes proceed either in the case of acetic acid or in that of propionic acid. The results indicating $C_2H_6$ and $CO_2$ as the principal products of the photolysis of aqueous propionic acid solutions, show that even in that acid the primary step may be mainly through the rearrangement mechanism and that the rupture process may be relatively rare, although much more frequent than in the case of acetic acid.

This type of result, in which the yield of free radicals or free atoms per einstein absorbed increases with the length of the carbon chain, may be rather general. It is in line with the observation that formaldehyde gives only stable molecules on photolysis[14] whereas acetaldehyde decomposes both by rupture and by rearrangement.[15] The extension of this work to longer carbon chains and different types of compounds may prove quite interesting.

It was shown in Part II that the activation energy of reactions involving the disappearance of atomic hydrogen (presumably reaction 6) decreases as we pass from acetic acid to propionic acid; this may indicate a diminution in the strength of the R–C bond as we proceed to longer chain acids. It is important, however, to note that the calculations for the amount of atomic hydrogen produced in the irradiated zone are valid regardless of the reaction assumed for its disappearance.[16]

The results of Part IV verify the earlier conclusion of Burton that acetic acid does not decompose by reaction (8) to any marked extent.[5] Taken together with Part I and the earlier work on formic acid,[2,3] it fairly well indicates that the reaction

$$RCOOH + h\nu \longrightarrow RCO + OH \qquad (10)$$

---

[13] Spence and Wild, *J. Chem. Soc.*, 352 (1937).

[14] Löcker and Patat, *Z. physik. Chem.*, **B18**, 124 (1932). In later publications, Patat, *ibid.*, **B25**, 208 (1934), and Löcker and Patat, *ibid.*, **B27**, 431 (1934), presented evidence for the production of free H atoms at < 2700 Å.

[15] Blacet and Roof, THIS JOURNAL, **58**, 278 (1936); Rollefson, *J. Phys. Chem.*, **41**, 259 (1937); Burton, *ibid.*, **41**, 322 (1937).

[16] A slight error is introduced, however, by neglect of the effect of particle size on the number of impacts suffered by a hydrogen atom.

does not occur in any photolyses in the quartz region. The free hydroxyl radicals reported by Terenin and Neujmin[17] in the photolysis of formic and acetic acids may perhaps be due to some such series of reactions as previously suggested by Burton. On the other hand, it should be noted that in the region of the spectrum employed by Terenin and Neujmin (~1560 Å.) it is possible that the primary process is different from that of the photodecomposition in the range used in this investigation. At any rate it is well to bear in mind that excited free OH radicals may be detected by their emission spectrum in traces which may be too small to be of chemical significance.

## Summary

1. The photolysis of the aliphatic acids (except formic acid) may proceed either via a rupture involving the formation of atomic hydrogen or via a rearrangement mechanism yielding ultimate molecules in the primary act.

2. In the cases of both acetic and propionic acid, the rearrangement mechanisms are possibly predominant.

3. Per einstein absorbed, rupture takes place at least 2.3 times as frequently in the case of propionic acid as in that of acetic acid.

4. The energy of activation of the reaction by which hydrogen atoms disappear in acetic acid has been redetermined to be 8.5–9.9 kcal., in good agreement with that calculated from previous results.

5. The energy of activation of the similar reaction in propionic acid has been found to be ~0.8 kcal. less. This may indicate a weakening in the C–C bond at the COOH radical with increase in length of the carbon chain.

6. Neither alkyl nor RCO radicals appear to be formed in the photolysis of acetic or propionic acid.

UNIVERSITY HEIGHTS
NEW YORK, N. Y.
BERKELEY, CALIF.

RECEIVED JANUARY 26, 1938

---

(17) Terenin and Neujmin, *J. Chem. Phys.*, **3**, 436 (1935); Terenin, *Acta Physicochim. U. R. S. S.*, **3**, 181 (1935).

---

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 633]

# The Coördination of Silver Ion with Unsaturated Compounds

BY SAUL WINSTEIN AND HOWARD J. LUCAS

One of the interesting properties of substances having an ethylenic linkage is the ability to form compounds of comparatively low stability. Such compounds are best termed "addition" or "coördination" compounds. They are distinctly different in type from the stable addition compounds produced by the action of the usual reagents, such as the halogens. Some compounds previously described probably belong to the coördination type, for example, the complex salts of hydrocarbons with aluminum and ferric chlorides,[1] the loose addition compounds of olefins with (a) hydrogen bromide, of the type $C_2H_4\cdot HBr$,[2] (b) zinc chloride, of the type $C_5H_{10}\cdot ZnCl_2$[3] and the addition compounds of aromatic hydrocarbons with nitro compounds.[4] In the complex iron compound, $FeC_4H_6(CO)_3$, in which two of the five molecules of carbon monoxide of iron carbonyl are replaced by one molecule of butadiene, the unsaturated hydrocarbon satisfies one or two coördination positions of the iron atom.[5]

Cuprous, silver, and mercury salts are used for absorbing olefins.[6,7] Ethylene appears to form a loose chemical compound with cuprous chloride.[8] Addition compounds of olefins with platinous halides of the types $PtCl_2\cdot C_2H_4$ and $KPtCl_3\cdot C_2H_4$, known for over a century,[9] have been the subject of renewed interest lately.[10]

An understanding of the nature of the coördination bond in these olefin–metal complexes requires additional data. In this investigation, a

---

(1) (a) Henderson and Gangloff, THIS JOURNAL, **39**, 1420 (1917); (b) Hunter and Yohe, *ibid.*, **55**, 1248 (1933); (c) Egloff, Wilson, Hulla and Van Arsdell, *Chem. Rev.*, **20**, 345 (1937).

(2) Maass and Wright, THIS JOURNAL, **46**, 2664 (1924).

(3) Kondakow, *Chem. Listy*, **24**, 1 (1930).

(4) Taylor and Baker, "Sidgwick's Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, p. 264.

(5) Reihlen, *Ann.*, **482**, 161 (1930).

(6) Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, N. Y., 1934, pp. 142, 582.

(7) Eberz, Welge, Yost and Lucas, THIS JOURNAL, **59**, 45 (1937).

(8) Manchot and Brandt, *Ann.*, **370**, 286 (1911).

(9) Zeise, *Pogg. Ann.*, **21**, 497 (1831); Birnbaum, *Ann.*, **145**, 67 (1868).

(10) (a) Pfeiffer and Hoyer, *Z. anorg. allgem. Chem.*, **211**, 241 (1933); (b) Anderson, *J. Chem. Soc.*, 971 (1934); (c) Anderson, *ibid.*, 1042 (1936); (d) Kharasch and Ashford, THIS JOURNAL, **58**, 1733 (1936).