Monolupine Dihydrochloride.—Five grams of monolupine in 15 cc. of acetone treated with 5 cc. of concd. hydrochloric acid (excess) produced a sirupy precipitate which was redissolved by the addition of just enough alcohol. After standing in an ice box for two hours the mixture solidified to a mush of crystals, which was filtered, washed with acetone and recrystallized from alcohol–acetone as fine white plates. Dried over calcium chloride the m. p. was 115–116° with rapid heating. Slower heating gave various results due to decomposition. When heated at 100° the dihydrochloride loses 2 moles of water and 1 mole of hydrochloric acid being converted into the monohydrochloride. The loss varies with the efficiency of the drying over calcium chloride.

Anal. Calcd. for $B \cdot 2HCl \cdot 2H_2O$, (367.2): Cl, 19.33; moisture (1 HCl plus $2H_2O$), 19.74%. Found: Cl, 19.6; moisture, 20.24, 20.25. $(\alpha)^{29}\mathrm{D}$ $-120.3°$ in water, $c = 2.1620$, $l = 2$, $a = -5.20°$.

Monolupine Hydrochloride.—Prepared by heating the dihydrochloride at 110° to constant weight as white powder, very hygroscopic, m. p. 280°. It could not be recrystallized.

Anal. Calcd. for $B \cdot HCl$, (294.7): Cl, 12.05. Found: Cl, 12.06, 12.09.

Monolupine Gold Chloride.—To a solution of the dihydrochloride in water was added an excess of gold chloride solution. The yellow curdy precipitate was redissolved by heating and the filtered solution was set aside. On cooling a mass of yellow needles separated. These were filtered off, and dried; m. p. 167–168° (dec.). The mother liquor deposited a film of metallic gold after standing for twenty-four hours.

Anal. Calcd. for $B \cdot 2HAuCl_4 \cdot 3H_2O$, (992.6): Au, 39.73; H_2O, 5.44. Found: Au, 39.70; H_2O, 5.46.

Monolupine Methiodide.—Two grams of monolupine in 5 cc. of acetone mixed with 2 cc. of methyl iodide deposited crystals after two days of standing. These were recrystallized from alcohol twice and dried when the m. p. was constant at 257°.

Anal. Calcd. for $B \cdot CH_3I \cdot H_2O$ (418.2): I, 30.33; H_2O, 4.30. Found: I, 30.83, 30.85; H_2O, 4.06, 4.03.

Summary

Lupinus caudatus Kellogg contains 0.44 to 0.45 % of a new alkaloid, monolupine, $C_{16}H_{22}ON_2$, that closely resembles anagyrine. Chemically this plant is distinct from *L. palmeri*.

WASHINGTON, D. C. RECEIVED MARCH 2, 1936

NOTES

The Preparation of Platinum Oxide for Catalytic Hydrogenations

BY WILLIAM F. BRUCE

Platinum oxide for catalytic hydrogenations can be prepared more conveniently from ammonium chloroplatinate than from chloroplatinic acid by the well-known procedure of Adams.[1] By adding an excess of ammonia to a solution of chloroplatinic acid, ammonium chloroplatinate is precipitated. This is the basis for a convenient method of recovering platinum in spent catalysts.[2] The amount of catalyst produced from a given weight of ammonium chloroplatinate is almost exactly one-half the weight of the ammonium salt and is therefore very easily calculated. Ammonium chloroplatinate is not hygroscopic and is therefore weighed more easily than chloroplatinic acid. In starting from the ammonium salt, no water is used, and hence no spattering occurs in heating the mixture to the fusion temperature.

By the new procedure a given weight of ammonium chloroplatinate is well mixed with ten times its weight of powdered sodium nitrate, and the mixture is heated gradually to the fusion point. During this process much gas is evolved, due presumably to the decomposition of ammonium nitrate, but the evolution is gentle and no spattering occurs. The fused mixture is held at 500° for twenty-five to thirty minutes and the platinum oxide is isolated according to Adams' directions. From 3.0 g. of the salt was obtained 1.51 g. of platinum oxide, no different in general appearance or activity from that prepared in the usual way. This experiment has been duplicated in several other laboratories and shortens the procedure for converting spent catalyst to platinum oxide by 25% or more.

The following data which compare the rates of hydrogenation of maleic acid and of benzaldehyde using catalysts prepared by the original (I) and by the modified (II) procedures were communicated by Dr. E. L. Baldeschwieler and are reported with his permission.[3]

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(1) Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Collective Vol. I, 1932, p. 452.

(2) Baldeschwieler and Mikeska, THIS JOURNAL, **57**, 977 (1935).

(3) Catalyst II used in these experiments was prepared by adding ammonium chloroplatinate in small portions to fused sodium nitrate at 350° rather than by the more convenient procedure described above since this method was developed later.

TABLE I

A. HYDROGENATION OF MALEIC ACID

Hydrogen absorbed, cc.	Total time, seconds Catalyst I (original method)	Catalyst II (modified method)
100	78	60
200	123	98
300	166	135
400	208	173
500	249	213
600	288	253
B. HYDROGENATION OF BENZALDEHYDE[4]		
100	70	152
200	125	239
300	181	314
400	240	388
500	304	465
600	372	545

These results show that the catalyst prepared by the modified procedure was in this case somewhat better for the hydrogenation of maleic acid than that made in the usual way, while the reverse is true for the hydrogenation of benzaldehyde. Reference to the previous study of rates of hydrogenation by this same technique[2] shows that the catalysts reported here are even more active than those in the earlier work.

[4] The addition of a trace of $FeSO_4$ sometimes promoted the reaction and sometimes poisoned it.

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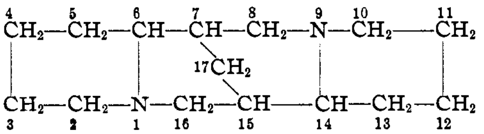
RECEIVED MARCH 5, 1936

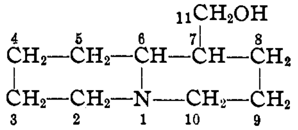
The Numbering of the Sparteine Molecule and its Derivatives

BY JAMES FITTON COUCH

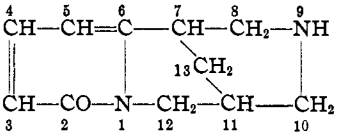
The constitution of sparteine as modified by Clemo and Raper [*J. Chem. Soc.*, 644–645 (1933)] from the structure suggested by Ing [*ibid.*, 504–510 (1933)] may be rearranged to the following form, and the component atoms may then be



numbered in the fashion indicated beginning with a ring nitrogen atom in the conventional way. It would be more convenient in this particular case to start with carbon atom number 16 but it is better to adhere to the established rule. This arrangement of the sparteine formula which has been accepted by Prof. Clemo [personal communication] shows at once its symmetrical character and relationship to other lupine alkaloids and to cytisine and anagyrine. Lupanine becomes 2-keto-sparteine, hydroxylupanine tentatively its 10-hydroxy derivative and anagyrine is 3,4,5,6-tetradehydro-2-keto-sparteine. Lupinine may be formulated as



and cytisine



indicating a close relationship between these alkaloids since cytisine may be derived from (hypothetical) tetradehydro-2-keto-lupinine by condensation of methylamine across atoms 9 and 11 of the lupinine skeleton, atom 8 becoming atom 13 of cytisine. Sparteine may be theoretically derived from lupinine by condensation with piperidine in an analogous manner.

BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.

RECEIVED MARCH 2, 1936

Amino Alcohols Derived from 1,2,3,4-Tetrahydrodibenzofuran

BY RICHARD A. ROBINSON AND ERICH MOSETTIG

In logical connection with a study of derivatives of 4,5-phenanthylene oxide [Mosettig and Meitzner, THIS JOURNAL, **56**, 2738 (1934)] the investigation of dibenzofuran derivatives was begun in this Laboratory in 1932 with the hope of finding in this series compounds resembling, particularly in their analgesic action, morphine. In our first paper dealing with dibenzofuran derivatives [Mosettig and Robinson, *ibid.*, **57**, 902 (1935)] we outlined in some detail the direction in which our further synthetic experiments were to proceed. In the meantime other research groups [Kirkpatrick and Parker, *ibid.*, **57**, 1123 (1935); Gilman, Smith, and Cheney, *ibid.*, **57**, 2095 (1935)] have approached the synthesis of possibly analgesic and hypnotic substances in the dibenzofuran series in a way which is in part similar to ours; previous publications from these investigators had not indicated any intention of seeking morphine-like substances. In order to avoid unnecessary duplication of effort, some of our recent experimental results are submitted in this preliminary form.

1,2,3,4-TETRAHYDRODIBENZOFURAN DERIVATIVES

Substance	M. p., °C. (corr.)	Formula	Analyses, % Calcd.	Analyses, % Found
7-ω-Bromoacetyl-	81–82	$C_{14}H_{13}O_2Br$	Br, 27.27	27.72
7-[2-(Dimethylamino)-1-oxo-ethyl]-hydrochloride	244–247	$C_{16}H_{20}O_2NCl$	Cl, 12.07 N, 4.77	12.06 4.73
7-[2-(Diethylamino)-1-oxo-ethyl]-hydrochloride	202–210	$C_{18}H_{24}O_2NCl$	Cl, 11.03 N, 4.35	11.11 4.19
7-[2-Piperidino)-1-oxo-ethyl]-hydrochloride	235–239	$C_{19}H_{24}O_2NCl$	Cl, 10.63 N, 4.20	10.65 4.59
7-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-oxo-ethyl]-hydrochloride	260–264	$C_{23}H_{24}O_2NCl$	N, 3.67	3.64
7-[2-(Dimethylamino)-1-hydroxy-ethyl]-hydrochloride	220–222	$C_{16}H_{22}O_2NCl$	C, 64.95 H, 7.50 Cl, 12.00	65.40 7.68 12.08
7-[2-(Piperidino)-1-hydroxy-ethyl]-hydrochloride	230–232	$C_{19}H_{26}O_2NCl$	C, 67.93 H, 7.81 Cl, 10.56	67.63 7.72 10.67
7-[2-(1,2,3,4-Tetrahydroisoquinolino)-1-hydroxy-ethyl]-hydrochloride	197–200	$C_{23}H_{26}O_2NCl$	C, 71.94 H, 6.83	71.85 6.94

The amino alcohols derived from 1,2,3,4-tetrahydrodibenzofuran which carry the alkamine side chain in position-7 were prepared by a method described in principle previously for the synthesis of their analogs in the dibenzofuran series itself [Mosettig and Robinson, *ibid.*, **57**, 2186 (1935)]. The constitutional proof for the starting material, 1,2,3,4-tetrahydro-7-acetyl-dibenzofuran, has been offered recently by Gilman, Smith, and Cheney (*l. c.*). Considerable difficulties have been encountered in the catalytic reduction of the amino ketones to the corresponding amino alcohols.

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RECEIVED FEBRUARY 19, 1936

A Note on Some Color Reactions of Hydroquinone in the Solid State

BY SIDNEY J. FRENCH AND DONALD J. SAUNDERS

J. Maldiney in 1914[1] reported briefly that colors of blue and gray were obtained when solid hydroquinone was mixed with solid alkali carbonates. He attributed the effect to the action of light and to a slight oxidation of the hydroquinone.

Further investigation of these color reactions by the writers has shown that they are dependent on the presence of small amounts of moisture, for the anhydrous salts give no color while the presence of an excess of water gives a yellow solution. A number of salts were used and it was noted (1) that only the more alkaline salts give colors and (2) the colors ranged from gray through blue and green to black, being roughly proportional to the increasing alkalinity of the compound used. Thus, trisodium arsenate and sodium tetraborate gave blue gray colors; sodium silicate and sodium cyanide, blue; sodium phosphate and sodium carbonate, blue green; and sodium hydroxide, black. Less alkaline salts such as sodium bicarbonate and disodium phosphate gave no colors. Salts showing colors were salts of acids having smaller ionization constants than that of hydroquinone in its primary ionization stage, while salts showing no color were those of acids having higher ionization constants than that of hydroquinone.

Dry buffer mixtures were prepared as indicated in Table I. The *p*H of the solution of each buffer mixture is shown together with the color produced when each dry buffer is mixed with an equal quantity of hydroquinone and placed in a desiccator over water. The results indicate the change in color with increasing alkalinity of the mixture and indicate the possibility of determining the approximate alkalinity of a substance in the solid state. Colors corresponding to various *p*H solution ranges would be as follows.

TABLE I

BUFFER MIXTURE COMPOSITIONS

	Parts by weight Compound	Parts by weight NaOH	*p*H of soln.	Color with hydroquinone
Glycine	5.5	4.5	10.4	No color
$Na_2HPO_4 \cdot 12H_2O$	2.69	0.060	10.97	Faint gray
$Na_2HPO_4 \cdot 12H_2O$	2.69	.100	11.29	Gray
$Na_2HPO_4 \cdot 12H_2O$	2.69	.200	11.77	Blue gray
$Na_2HPO_4 \cdot 12H_2O$	2.69	.300	12.06	Blue
Glycine	3.0	7.0	12.50	Blue green
Glycine	1.0	9.0	12.8–12.9	Green
None	...	solid	....	Black

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[1] J. Maldiney, *Compt. rend.*, **158**, 1782 (1914).

	*p*H
No color	10.5 or less
Gray to faint blue gray	10.5–11.5
Blue gray to blue	11.5–12.0
Blue to blue green	12.0–12.5
Blue green to green	12.5–13.0
Green to black	13.0–14.0

In addition to its function as a test for the relative alkalinity of moist solids, the color reaction serves as a convenient method for distinguishing between the alkali triphosphates and diphosphates since the latter give no color. It also distinguishes between alkali tri- and di-arsenates and between alkali carbonates and bicarbonates. The reaction can be used to identify hydroquinone. Neither catechol nor resorcinal show similar color reactions. Finally, the reaction may be used as a convenient test to indicate the presence or absence of moisture or water of hydration in an alkaline salt. The anhydrous salts show no color on grinding with hydroquinone; the color appearing only after the mixture stands over water. Hydrated salts show immediate color on grinding.

COLGATE UNIVERSITY
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RECEIVED FEBRUARY 3, 1936

Theoretical Considerations Concerning the Mechanism of the Thermal Reaction between Gaseous Iodine Monochloride and Hydrogen

BY ALBERT SHERMAN AND NORMAN LI

Bonner, Gore and Yost[1] made an experimental study of the reaction

$$2\,\mathrm{ICl}\ (g) + \mathrm{H_2}\ (g) = \mathrm{I_2}\ (g) + 2\,\mathrm{HCl}\ (g)$$

and suggested tentatively the following mechanism

$$\mathrm{H_2} + \mathrm{ICl} = \mathrm{HI} + \mathrm{HCl}\ \text{(slow)} \qquad (1)$$
$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2}\ \text{(rapid)} \qquad (2)$$

They found the energy of activation for the assumed slow reaction to be 33,900 cal.

We have calculated the energies of activation for the above two reactions in order to find out whether this mechanism is reasonable. The method used in the calculations was the so-called semi-empirical one of Eyring and his co-workers[2] and will not be discussed here. The various integrals involved were evaluated by constructing Morse potential energy curves for the bonds, the coulombic energy for every bond being taken as 14% of the total energy. The constants used in constructing the Morse curves are given

Bond	r_0	w_0	D
H–H	0.74[3]	4375[3]	102.4[3]
I–Cl	2.30[3]	385[4]	49.7[3]
H–Cl	1.28[5]	2840.8[5]	101.5[6]
H–I	1.62[5]	2233[7]	69.0[6]
I–I	2.66[3]	213.7[5]	35.4[8]

The first column gives the bond, the second the equilibrium distance in Å. between the two atoms, the third gives the vibrational frequency of the lowest state in cm.$^{-1}$, and the fourth the heat of dissociation of the bond in kg. cal.

The activation energy for the reaction

$$\mathrm{H_2} + \mathrm{ICl} = \mathrm{HI} + \mathrm{HCl}$$

is calculated to be 39 kcal. as compared with the experimental value of 33.9 kcal. The agreement is fairly good, and in general is about that to be expected for such calculations.

The activation energy of the reaction

$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2}$$

was found to be 41 kcal. This energy is 2 kcal. greater than that calculated for the first reaction. Although the calculated value for the activation energy of the first reaction disagrees with the experimental value by 5 kcal., nevertheless the difference between the energies calculated for the two reactions is probably much more reliable than this, and the 2 kcal. is therefore of significance, especially the sign of the difference.

It follows that in order for the mechanism postulated by Bonner, Gore and Yost to be correct, their reaction (2) must involve some mechanism other than a bimolecular one. We suggest the following

$$\mathrm{I_2} \rightleftharpoons 2\mathrm{I} \qquad (3)$$
$$\mathrm{I} + \mathrm{ICl} = \mathrm{I_2} + \mathrm{Cl} \qquad (4)$$
$$\mathrm{Cl} + \mathrm{HI} = \mathrm{HCl} + \mathrm{I} \qquad (5)$$

Equations (4) and (5) add up to equation (2), and equation (3) is the thermal dissociation of iodine. The over-all activation energy of the reaction

$$\mathrm{HI} + \mathrm{ICl} = \mathrm{HCl} + \mathrm{I_2}$$

with the above mechanism is equal approximately to the activation energy of reaction (4), calculated to be 16.3 kcal., plus one-half the heat of dissociation of iodine,[9] 17.9 kcal., or a total of 34.2 kcal.

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(1) Bonner, Gore and Yost, THIS JOURNAL, **57**, 2723 (1935).

(2) See, for example, Van Vleck and Sherman, *Rev. Modern Phys.*, **7**, 207 (1935).

(3) R. S. Mulliken, *ibid.*, **4**, 1 (1932).

(4) W. Jevons, "Report on Band Spectra of Diatomic Molecules," Physical Society, Camb., 1932.

(5) Weizel, "Bandenspektrum," Leipzig, 1931 (Hand. der Physik—Erganzswerk bd. 1).

(6) L. Pauling, THIS JOURNAL, **54**, 3570 (1932).

(7) K. W. F. Kohlrausch, "Der Smekal-Raman Effekt," J. Springer, Berlin, 1931.

(8) W. G. Brown, *Phys. Rev.*, **37**, 1007 (1931).

(9) Van Vleck and Sherman, *Rev. Modern Phys.*, **7**, 210 (1935).

The difference between the activation energies of the reactions

$$H_2 + ICl = HI + HCl \text{ and}$$
$$HI + ICl = HCl + I_2$$

is now calculated to be 4.8 kcal., with the former reaction having the larger value. If we assume the equation

$$k = aZe^{-E/RT}$$

and consider a and Z to be the same for the two cases the ratio of the specific reaction rate constants at 220° is

$$k_2/k_1 = e^{4800/986} = 130$$

where k_1 is the specific reaction rate constant for reaction (1) and k_2 is that for (2).

We wish to point out the usefulness of activation energy calculations in just such a case as this —to aid the experimental chemist in deducing a mechanism for a reaction, a problem which primarily involves a knowledge of the difference between two energies rather than their absolute values.

PHYSICAL CHEMICAL LABORATORY
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MADISON, WISCONSIN
RECEIVED FEBRUARY 24, 1936

Catalysis by Fusions: A Reply to the Paper by Adadurow and Didenko

BY E. W. R. STEACIE AND E. M. ELKIN

In a recent paper Adadurow and Didenko[1] have criticized our work on the decomposition of methanol on solid and liquid zinc.[2] The main points in their article are as follows.

(a) They cite experiments to show that the efficiency of a silver catalyst for the oxidation of ammonia falls abruptly *in the neighborhood* of the melting point. Actually, however, it is obvious from the data that the sharp decrease in activity occurs from 40 to 130° below the melting point of silver. Their catalyst was initially porous. Their experimental description is very ambiguous, and it is difficult to decide how the experiments were made, but it appears almost certain that they were performed in order of increasing temperature. Hence as the melting point was approached sintering occurred, with an accompanying reduction in the total surface and hence in the activity. The most striking thing about their data, however, is that in every case *the efficiency of the catalyst about the melting point is greater than that immediately below it.* Their data are therefore in complete agreement with our work rather than contrary to it as they suggest.

(b) In an attempt to show that a zinc oxide layer on the surface of molten (or solid) zinc was the real catalyst in our experiments, they state "The decomposition of methyl alcohol takes place according to Bone and Davies by the equation $CH_3OH = CH_4 + O$." This is an extraordinary statement since there has never been any evidence for such a mechanism, and it is always assumed that the reaction proceeds by either dehydration or dehydrogenation.[3]

(c) On the basis of the above mechanism they conclude that a zinc oxide layer formed from the oxygen resulting from the decomposition was the active catalyst in our investigation. They go on to say "The higher the temperature the more zinc oxide is being formed, and it is plain why the work of Steacie and Elkin demonstrates here an uninterrupted growth of activity with the increase of temperature."

In our work we realized the necessity of avoiding contamination by zinc oxide. The zinc used was purified, vacuum distilled, and finally reduced with hydrogen *in situ.* Furthermore, it always maintained its metallic luster throughout a series of experiments, and no trace of zinc oxide was ever observed. Adadurow and Didenko report the oxidation of zinc on the passage of methyl alcohol vapor at 360 to 400°. No great weight can be attached to this observation, however, in the absence of any experimental details to prove the rigorous exclusion of oxygen from the reaction system.

Since each of our catalysts was used for a series of runs, it follows from Adadurow and Didenko's explanation that there should have been a progressive increase in activity from run to run. Hence an increase in activity with increasing temperature could only have occurred if experiments were always made in order of increasing temperature. Actually, however, it was shown that experiments made in order of decreasing temperature (Series VI) gave the same result. Furthermore successive runs made at the same temperature (Series V) agreed within the experimental error. Similar results were obtained in later work.[4]

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[1] Adadurow and Didenko, THIS JOURNAL, **57**, 2718 (1935).

[2] Steacie and Elkin, *Proc. Roy. Soc.* (London), **A142**, 457 (1933).

[3] Bone and Townend, "Flame and Combustion in Gases," Longmans, London, 1927; Sabatier-Reid, "Catalysis in Organic Chemistry," D. van Nostrand Co., New York, 1922; Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929.

[4] Steacie and Elkin, *Can. J. Research*, **11**, 47 (1934).

It also follows from the mechanism proposed by Adadurow and Didenko that the (per cent. reaction)–(time) curve for a single experiment must be autocatalytic in nature, since the reaction is assumed to be proceeding on zinc oxide formed by the decomposition of the reactant. No such effect was found, as is shown by Figure 1 of our paper.

It appears therefore that the criticisms of Adadurow and Didenko are based partly on an incorrect interpretation of their own data, and partly on an incorrect mechanism for the decomposition of methyl alcohol. On this basis they arrive at an alternative explanation of our experiments which is not in accord with the facts.

PHYSICAL CHEMISTRY LABORATORY
McGILL UNIVERSITY, MONTREAL

RECEIVED JANUARY 21, 1936

COMMUNICATIONS TO THE EDITOR

THE PHOTOLYSIS OF ACETIC ACID

Sir:

In the course of a general investigation of the mechanism of the photolysis of acetic acid I applied the method of Paneth [*Ber.*, **62B**, 1335 (1929)] to the detection of free radicals. Using a light lead mirror followed in order by a heavy lead guard mirror and a light antimony mirror, approximately simultaneous disappearance of the two light mirrors was observed.

The efficacy of the guard mirror was checked by experiments with acetone. In a particular series of experiments, it was found that a guard mirror which was ineffective in preventing the removal of an antimony mirror in an acetic acid run was, after the lapse of a day, still effective in preventing such disappearance of a fresh antimony mirror in an acetone run, even though it itself was now visibly affected. The period of the latter run was equivalent (in free radical yield) to more than twice that of the acetic acid run. When, after the latter experiment, the guard mirror was reinforced by redeposition of lead, it was found that it was still ineffective in preventing the removal of the same antimony mirror in an immediately following run with acetic acid.

Except for the use of the guard mirror and the succeeding antimony mirror, the experiments bore a resemblance to those of Pearson [*J. Chem. Soc.*, 1718 (1934); *ibid.*, 1151 (1935)].

The effect on the lead mirrors may be attributed to the formation of free radicals, presumably methyl, and that on the antimony mirrors to the formation of atomic hydrogen in the photolysis of acetic acid in the vapor phase according to a mechanism

$$CH_3COOH + h\nu \longrightarrow CH_3 + COOH \quad (1)$$
$$COOH \longrightarrow CO_2 + H \quad (2)$$

Inasmuch as Farkas and Wansbrough Jones [*Z. physik. Chem.*, **B18**, 124 (1932)] offer good evidence [v. Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934)] for a primary formation of ultimate molecules according to the alternative mechanisms

$$CH_3COOH + h\nu \longrightarrow CH_4 + CO_2 \quad (3)$$
$$(CH_3COOH)_2 + h\nu \longrightarrow C_2H_6 + CO_2 + CO + H_2O \quad (4)$$

I am led to the conclusion that, in acetic acid, decomposition may occur either from a suitable constellation of atoms by rearrangement of bonds into equally stable constellations of other molecules or from a molecule of sufficient energy content into free radicals. The implications of this conclusion are being subjected to further test.

On the basis of the results of Pearson, Robinson and Stoddard, [*Proc. Roy. Soc.* (London), **A142**, 275 (1933)] the effect on the antimony mirror would have been unexpected since they report that the recombination of atomic hydrogen is catalyzed by a lead mirror. The results here indicate that at low concentrations of atomic hydrogen the recombination process is improbable. So far as known this is the first time that this method has been applied to the detection of hydrogen atoms in the presence of free radicals.

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RECEIVED FEBRUARY 24, 1936