NOTES

The Stability of the Free Formyl Radical

By Milton Burton

The stability of formyl has a direct bearing on the mechanism of reactions such as the decomposition of the aldehydes. In recent papers[1] indirect evidence has been cited relating to the possibility of the reaction

$$HCO \longrightarrow H + CO \qquad (1)$$

It consequently seems advisable to call attention to direct evidence on this point, which unfortunately has been published where it is obscured by other findings.

The evidence is of two kinds. Incidentally to a paper on the photolysis of formic acid,[2] it has been shown by the use of the guard mirror method[3] that, although CH_3 radicals are formed in the photolysis of acetaldehyde, no H atoms are produced. Since part at least of the primary reaction must be by the path

$$CH_3CO \longrightarrow CH_3 + HCO \qquad (2)$$

this is equivalent to the statement that the HCO radicals so formed do not decompose at 100° (which was the temperature of the test) but enter some other reaction, *e. g.*

$$2HCO \longrightarrow H_2 + 2CO \qquad (3)$$

The objection may be made that the lead guard mirror itself prevents the passage of HCO radicals but that is beside the point. The HCO radicals have ample time to dissociate before they reach the lead mirror. If any H atoms are formed, the antimony mirror would detect them.[3] The failure to detect such atoms by this sensitive method is very pertinent.

In some comments on a paper by Rollefson[4] the writer[5] presented other evidence on this point. Calculations from data by Leighton and Blacet[6] and Blacet and Roof[1a] were used to establish the fact that if hydrogen atoms are formed in the photolysis of acetaldehyde they take no further part in the reaction or, which is more probable, that no hydrogen atoms are formed.

It is interesting to note that the stability of HCO has been established from two distinctly different types of experiments (one involving direct test, the other kinetic studies) and that the radical appears to be stable even at 100°. This stability is to be compared with that of the CH_3CO radical which, according to Spence and Wild,[7] is stable at room temperatures but is completely decomposed at 60°.

(1) (a) Blacet and Roof, This Journal, **58**, 278 (1936); (b) Leighton, Levanas, Blacet and Rowe, *ibid.*, **59**, 1843 (1937); (c) Blacet, Fielding and Roof, *ibid.*, **59**, 2375 (1937).

(2) Burton, *ibid.*, **58**, 1655 (1936).

(3) Burton, *ibid.*, **58**, 1645 (1936).

(4) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

(5) Burton, *ibid.*, **41**, 322 (1937).

(6) Leighton and Blacet, This Journal, **55**, 1766 (1933).

(7) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

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Reaction Vessels for Pressure Experiments[1]

By Aristid V. Grosse

There are a great number of chemical reactions which cannot be studied at elevated or high pressures in the usual type of apparatus because their material is either attacked by reagents or catalyzes the reactions investigated in an undesirable manner. Such material is practically always iron in the form of steel or ferrous alloys. On the other hand, the usual corrosion-resistant and non-catalytic materials are unsuitable for constructing high pressure apparatus because they lack tensile strength and other necessary mechanical properties.

The following simple type of reaction vessels equipped with a capillary, as illustrated in Fig. 1, and inserted into a cylindrical Ipatieff high pressure autoclave,[2] allows circumvention of these difficulties. It is based on the fact that the diffusion of gases and vapors through capillaries is extremely slow under pressure. Furthermore, the capillary provides a resistance to sudden mass flow from or into the vessel, but at the same time this resistance does not prevent pressure differences between the outside and inside of the reaction vessel from equalizing fairly rapidly, so that gases can be readily pressed in or released from the vessel. By choosing suitable capillary dimensions

(1) Presented before the Division of Organic Chemistry, at the Rochester Meeting, Sept., 1937, of the American Chemical Society.

(2) As shown in Fig. 1, This Journal, **57**, 1618 (1935).

and providing sufficient pressure in the autoclave by means of an inert gas,[3] usually nitrogen, the losses from the liner can be limited to negligible quantities. (Under "sufficient pressure of an inert gas" pressure substantially higher than the total pressure of the reacting chemicals is understood.)

The total losses from such vessels, due either to *diffusion* or more generally to *mass flow*, vary to a great extent and depend, outside of factors just mentioned, *i. e.*, length and diameters of capillaries, total pressure and mass density of reactants, also on temperature, rate of heating or cooling, nature of the reactants[4] and the inert gas, nature of the reaction itself (whether violent or smooth, exo- or endothermic, connected with pressure increase or decrease, etc.), ratio of pressure of reactants to pressure of inert gas and a few other less important factors.

In the more limited case of a pure inert liquid heated in an inert gas the losses from a capillary vessel during the usual procedure of experimentation may be attributed logically to three distinct periods (1) the time during which the autoclave is being heated, (2) the time during which the temperature is being kept constant or the actual diffusion period and (3) the time during which the autoclave is being cooled. By a proper technique the losses during periods 1 and 3, due *entirely* to mass flow, can be avoided practically completely.

For instance in Period 1 this is accomplished if the *rate of inert gas* input is so adjusted (for example by a precision needle valve) that it *always* remains *higher* than the rate of gas or vapor pressure increase of the reactants. In practice such an adjustment is not necessary in the numerous cases when a reaction takes place with gas absorption (for instance in hydrogenations or alkylations and polymerizations with gaseous olefins) because then the mass flow is only inward, into the capillary vessel. In Period 3 the gas flow will also be inward, since the vapors in the capillary vessel will condense more rapidly than the gas outside, except when the rate of cooling is too rapid.

An *example of losses* occurring during Period 2 is given in Table I.[5]

TABLE I

Run	Diffusion time, hrs.	Temp. of run, °C.	Total av. pressure, (C_6H_6 & N_2) kg./cm.[2]	Diffusion per hr. in mg.	Loss in weight, % of total benzene/hour
1	2.7	303	105	57	0.14
2	4.1	309	107	53	.13
3	8.0	314	111	53	.13
4	19.5	317	111.5	40	.10

In each experiment 41.1 g. of *pure benzene* (crit. temp. 289°, press. 48 atm.) was heated in a vessel of 137.3 cc. volume, with a capillary 41.7 cm. long and 0.646-mm. bore. Nitrogen was used as the inert gas. To decrease losses it is preferable to work *substantially* below the critical densities. In our case the density of benzene vapors (=0.299) was very near its critical density (=0.305). We see, however, that even under these conditions the losses are small—of the order of 0.1% per hour. For this reason high pressure experiments can be performed *quantitatively with great ease*, since all reagents, except gases pressed in or released from the autoclave, *will be found in the capillary vessel* and can be weighed accurately before and after each

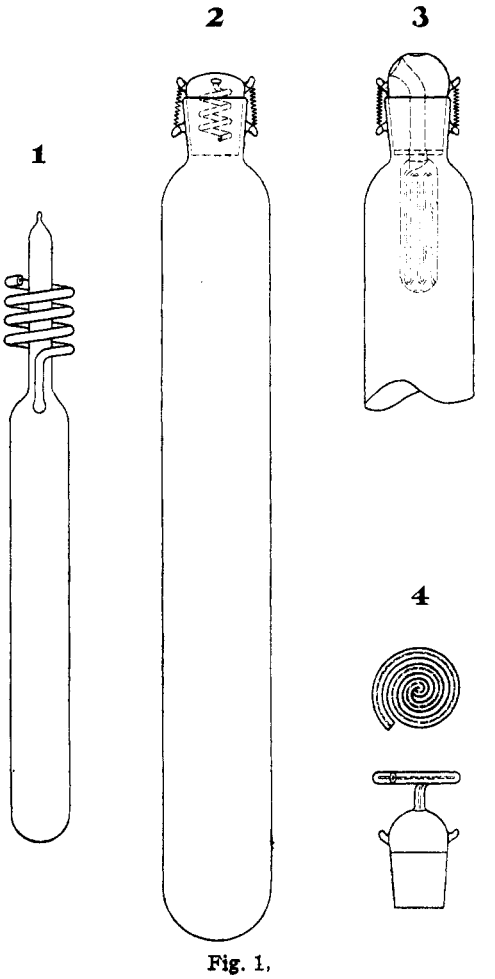

Fig. 1.

(3) Under the term "inert gas" any reacting gas may also be understood provided it is inert toward the autoclave material.

(4) In case of subliming substances care should be taken to avoid clogging of the capillary. As a precaution against clogging due to any cause one should either seal on a thin walled tube to the glass reaction vessel, which can be readily broken inside the autoclave, or use ground-in joints with springs, as illustrated in Fig. 1.

(5) See Dissertation of Leroy A. Johnson, Dept. of Chem., Univ. of Chicago, Aug., 1932.

reaction. With a little experience it is simple to adjust the inert gas pressure, length and bore of capillary desired in a particular experiment.

The practical advantages of the capillary vessels are evident from the fact that they have been used now for a period of over six years at the Riverside laboratories in thousands of experiments on many miscellaneous reactions, up to temperatures of 500° and pressures up to 500 atmospheres. The vessels had a capacity from 20 cc. up to about 3 liters. The capillaries ranged in length from 5 to 50 cm. and in bore from 0.1 to 2.0 mm. The usual material of construction was glass, but fused quartz, copper, nickel and other metals were also used.

In principle the method is not limited to capillaries and in industrial practice capillary spaces may be used to advantage.[6]

(6) See A. V. Grosse, U. S. Patent 1,986,196.

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Supplement to a Recent Paper on the Paramagnetism of Semiquinones

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The results obtained by a potentiometric method[1] concerning the structure of a quinhydrone in the dissolved state, with phenanthrenequinone-3-sulfonate as a model, recently were confirmed by the measurement of the paramagnetic susceptibility.[2] The method was based on the change of susceptibility of the solution of the quinone while it is slowly being reduced. This method had thus far to be restricted to strongly alkaline solutions, in which glucose could be used as a slowly acting reducing agent. We have succeeded now in finding an agent of similar properties for acid solutions. According to the potentiometric method, the quinhydrone of the dye mentioned, when produced in acid solution, is essentially a valence saturated dimeric compound. This result is now confirmed by the magnetic method.

The method is based on a reaction, clarified in detail by Smythe,[3] who showed that methylglyoxal in the presence of potassium cyanide as catalyst is a reducing agent. The rate of the reduction exerted on a reducible substance depends on the concentration of potassium cyanide and can be regulated by a proper choice of this concentration. In absence of oxygen or any other reducible substance, one molecule of methylglyoxal is reduced to a substance of a structure not yet fully known, probably a polymerization product, at the expense of another molecule which is oxidized to pyruvic acid. In the presence of another reducible substance of a potential range not more negative than that of indigo disulfonate, this substance is reduced while methylglyoxal is oxidized to pyruvic acid. This reaction can be used at any pH <7. In alkaline solution methylglyoxal is converted rapidly to lactic acid and so becomes ineffective for the reaction wanted.

Methylglyoxal can now be prepared easily by oxidation of acetone with selenium dioxide.[4,5] It is best stored in the form of a one molar aqueous solution and can be kept in the ice-box for several weeks.

A typical experiment follows: 0.1214 g. of potassium phenanthrenequinone-sulfonate and 0.0145 g. of potassium cyanide are dissolved in 5 cc. of acetate buffer (0.1 M in acetic acid and 0.1 M in sodium acetate), made up to a volume of 10 cc. with a 0.5 M aqueous solution of methylglyoxal, and sucked into the container of the magnetic balance. Before the first reading could be taken reduction, recognizable by the brown color, had already begun. The readings were continued until the complete discharge of color was reached, and longer. The change of volume susceptibility was

Time after mixing, min.	Volume susceptibility $K \times 10^6$	$\Delta K \times 10^6$	Color
17	0.72108	0.00014	Distinctly brown
20	.72103	.00019	
30	.72110	.00012	
34	.72108	.00014	
49	.72112	.00010	
71	.72122	.00000	Brown
77	.72122	.00002	Lighter brown
89	.72122	.00000	Fading
111	.72121	.00001	Colorless
127	.72122	.00000	

As stated in the previous paper, the limit of error may be estimated as 0.0002×10^{-6}. The changes are, accordingly, just within the limits of error. Since, however, this very slight change was observed also in a duplicate experiment, it may be real. If it be here also permitted to neglect all

(1) L. Michaelis and E. S. Fetcher, THIS JOURNAL, **59**, 2460 (1937).
(2) L. Michaelis, G. F. Boeker and R. K. Reber, *ibid.*, **60**, 202 (1938).
(3) C. V. Smythe, *Biochem. Z.*, **257**, 372 (1933).
(4) Hahn and Schales, *Ber.*, **67**, 1816 (1930).
(5) Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932).