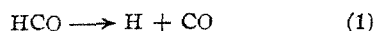


## NOTES

**The Stability of the Free Formyl Radical**

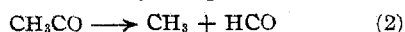
BY MILTON BURTON

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

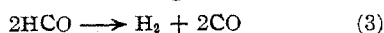


It consequently seems advisable to call attention to direct evidence on this point, which unfortunately has been published where it is obscured by other findings.

The evidence is of two kinds. Incidentally to a paper on the photolysis of formic acid,<sup>2</sup> it has been shown by the use of the guard mirror method<sup>3</sup> that, although  $\text{CH}_3$  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



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.*



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.<sup>3</sup> The failure to detect such atoms by this sensitive method is very pertinent.

In some comments on a paper by Rollefson<sup>4</sup> the writer<sup>5</sup> presented other evidence on this point. Calculations from data by Leighton and Blacet<sup>6</sup> and Blacet and Roof<sup>1a</sup> 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

(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).

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  $\text{CH}_3\text{CO}$  radical which, according to Spence and Wild,<sup>7</sup> is stable at room temperatures but is completely decomposed at 60°.

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

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**Reaction Vessels for Pressure Experiments<sup>1</sup>**

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,<sup>2</sup> 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).