

liquids expand on mixing. It does not necessarily follow that  $TS^E$  will be zero if the liquids are mixed at constant volume, though this might be the case if  $W$  had spherical symmetry.

We wish to thank Dr. H. C. Eckstrom of this Laboratory for the opportunity of discussing this paper with him.

### Summary

An apparatus is described for use in making

vapor-liquid equilibrium measurements and the conditions under which it gives accurate results have been ascertained. The excess thermodynamic functions for mixtures of ethylene bromide with (1) chlorobenzene and (2) 1-nitropropane have been measured. Experimental data now available indicate that the excess entropy change and the volume change on mixing possess the same sign. A possible explanation for this is given.

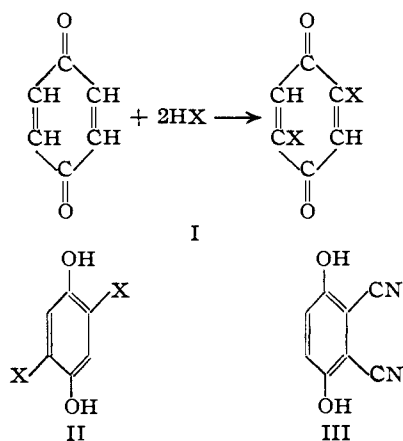
PROVIDENCE, RHODE ISLAND RECEIVED APRIL 12, 1941

## NOTES

### The Mechanism of the Addition of Hydrogen Cyanide to Benzoquinone

BY C. F. H. ALLEN AND C. V. WILSON

The addition of two molecules of unsymmetrical reagents to benzoquinone almost always gives rise to a substituted quinone (I) in which the new groups are on opposite sides of the benzene ring and in the 2,5-positions.

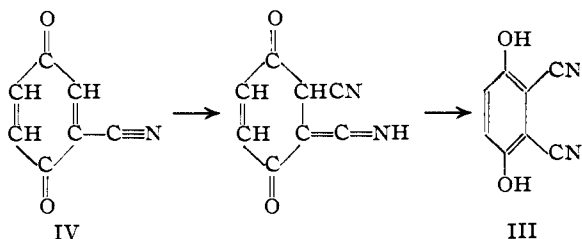


Sometimes the corresponding hydroquinone (II) results. The commonly accepted mechanism<sup>1</sup> accounts for the formation of this type of product by assuming consecutively 1,4-addition, enolization, and oxidation, the processes being repeated one or more times, depending upon the nature of the reactants.

An exception is encountered when hydrogen cyanide is the reagent of the type HX, used as an

addend. In this instance, two molecules add; the product is a dicyanohydroquinone (III),<sup>2</sup> in which both CN groups are adjacent and on the same side of the molecule, *i. e.*, unsymmetrical addition has occurred. No intermediates can be isolated; the only other product of the reaction is hydroquinone. The mechanism cannot be the same, therefore, when this reagent is employed.

However, an explanation becomes evident when the available unsaturated systems are examined. Addition of the first molecule of hydrogen cyanide takes place as with all HX-type reagents,<sup>1</sup> and the cyanoquinone is oxidized by the excess quinone to form a monocyanoquinone (IV). This cyanoquinone now contains an alternate conjugated system involving the nitrile group, to which hydrogen cyanide would be expected to add more readily than to the system  $C=C-C=C=O$ .<sup>3</sup> The resulting substance would be 2,3-dicyanohydroquinone (III), which is actually obtained. This suggested mechanism is, thus, in accord with the



known facts about the behavior of conjugated systems. It successfully accounts for the nature of the product and eliminates the apparent ex-

(1) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 800.

(2) Thiele and Meisenheimer, *Ber.*, **33**, 675 (1900).

(3) Duff and Ingold, *J. Chem. Soc.*, 87 (1934).

ception to the general mode of addition of reagents of the type HX to quinones.

Although not emphasized in the original literature,<sup>2,4</sup> the addition of hydrogen cyanide to benzoquinone is very sensitive to the temperature. It is essential to operate between 20 and 30° to secure any 2,3-dicyanohydroquinone. Neither we nor Graves and Adams<sup>5</sup> have been able to obtain any product by Helferich's procedure.

(4) German Patent 117,005 [*Frdl.*, VI, 113 (1900-1902)]; Helferich, *Ber.*, **54**, 155 (1921).

(5) Graves and Adams, *THIS JOURNAL*, **45**, 2447 (1923).

CONTRIBUTION NO. 804

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ROCHESTER, NEW YORK

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### The Activation of Aromatic Halogen

BY RICHARD BALTZLY AND JOHANNES S. BUCK

Some attempts to produce alkyl-*p*-bromoarylamines by direct alkylation of *p*-bromoarylamines failed and the trouble was traced to the action of the hydrobromic or hydriodic acid produced in the reaction, on the *p*-bromoarylamine.

Subsequent work showed that the bromine was unexpectedly mobile. Thus, *p*-bromoaniline, refluxed with hydriodic acid (57%), with red phosphorus to suppress the iodine produced, gave a 92% yield of aniline.

The action of hydrobromic acid was less complete. *p*-Bromoaniline heated with hydrobromic acid (48%), preferably at 150° under pressure, gave considerable amounts of aniline and 2,4-dibromoaniline, the over-all effect being that of a disproportionation.

The writers are not pursuing this line of research, since effectively the same subject is being studied in other laboratories.

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TUCKAHOE, N. Y.

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### Note on the Theory of Displacements of Mixtures Giving Maximum Flame Velocities\*

BY A. R. T. DENUES

It was indicated recently<sup>1</sup> that in the slow propagation of flame for both types of ordinary combustible gases apparently continuous relations exhibiting maxima exist between the displacements toward excess combustible of mixtures giving

\* Work done in the Department of Chemical Engineering of the University of Maryland. Original manuscript received August 16, 1940.

(1) Denués with Huff, *THIS JOURNAL*, **62**, 3045 (1940).

ing maximum flame velocity and the content of oxygen in the atmosphere used for premixing. The following development accounts for these effects and seems an interesting illustration of the present utility of the inadequate thermal theory.<sup>2</sup>

The displacement was early ascribed to dissociation<sup>3</sup> and to opposing effects of temperature and thermal conductivity,<sup>4</sup> but it has been treated more successfully by the elaborated thermal theory.<sup>5,6</sup> The present development is based on the generalized Nusselt equation as derived by Jahn.<sup>6</sup> This equation gives the flame velocity as a product of factors representing reaction velocity and thermal effects; its use introduces all lacks of the thermal theory.

According to this theory, the displacement results from competition between these factors representing reaction velocity and thermal effects, and specifically between a reaction velocity factor demanding maximum flame velocity with a great excess of combustible, except for combustion with pure oxygen, and the thermal effects demanding maximum flame velocity near equivalence. This view may be extended to include the weights of the two factors, comprising constituents representing magnitude and position.

If it be assumed that the weight of the thermal factor is substantially constant regardless of the composition of the atmosphere used and that it attains its maximum with a mixture near equivalence, the magnitude of the displacement will depend largely on the weight of the factor for reaction velocity, abbreviated *W*; the displacements will then exhibit a maximum coinciding with any maximum in *W*.

Such a maximum in *W* is seen if its constituents be viewed, from the equation cited, as a mass action product and as a function of *a*, the volume-fraction of oxygen in the atmosphere used, that affects the content of combustible for maximum flame velocity not directly but through its contributions to the absolute magnitude of the factor for reaction velocity: the constituent of position is given by divergences *d* between curves representing contents of combustible for maximum mass action product and for equivalence. As the factor for reaction velocity has for hy-

(2) For discussions see Lewis and von Elbe, *Chem. Rev.*, **21**, 347 (1937) and Coward and Payman, *ibid.*, **21**, 359 (1937).

(3) E. Mallard, *Ann. Mines*, [7] **7**, 355 (1875).

(4) Mallard and Le Chatelier, *ibid.*, **4**, 274 (1883).

(5) William Payman, *J. Chem. Soc.*, **117**, 48 (1920).

(6) Georg Jahn, "Der Zündvorgang in Gasgemischen," R. Oldenbourg, Berlin, 1934.