1,2,3,4-TETRAHYDRODIBENZOFURAN DERIVATIVES

Substance	M. p., °C. (corr.)	Formula	Analyses, % Calcd.	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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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	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).

	pH
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.

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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[8]
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

$$\mathrm{I_2} \rightleftarrows 2\mathrm{I} \qquad (3)$$

$$\mathrm{I} + \mathrm{ICl} = \mathrm{I_2} + \mathrm{Cl} \qquad (4)$$

$$\mathrm{Cl} + \mathrm{HI} = \mathrm{HCl} + \mathrm{I} \qquad (5)$$

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).