

over which equation (2) fits the data best. It is significant that over the temperature and pressure range studied equation (3) gives a maximum deviation of 1.9% as compared with 6.7% for equation (2) and 20.0% for equation (1), the three maximum deviations occurring at -70° and 100 atmospheres. The over-all behavior of the gas is represented best by equation (3).

It appears from this study that in the case of gases which, like nitrogen, obey the law of corresponding states fairly well, equation (3) has an advantage over other forms of Dieterici's equation heretofore used. Equation (3) does not possess the accuracy of equations of state with several adjustable constants, such as the Beattie-Bridgeman equation. It does, however, retain the theoretical advantage of Dieterici's original equation, since it has only two constants in addition to the gas constant, and since these constants may be eliminated in terms of the critical constants, giving a reduced equation of state.

TABLE II

DEVIATIONS OF CALCULATED FROM OBSERVED PRESSURES FOR NITROGEN^a

Temp., °C.	Eq. (1)	Eq. (2)	Eq. (3)
-70	11.47	3.32	1.29
-50	9.76	2.08	0.71
-25	8.21	1.18	.29
0	7.02	0.62	.03
20	6.22	.31	.16
50	5.29	.09	.32
100	4.07	.36	.53
200	2.69	.49	.56
300	1.94	.50	.53
400	1.35	.51	.53
500	0.98	.51	.53
600	.73	.49	.49

Total av. % dev. 4.98 .87 .50

^a The value entered for each temperature is the average of the per cent. deviations of the calculated from the observed pressures at 20, 40, 60, 80, and 100 atmospheres.

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Kinetics of Development by Catechol

By T. H. JAMES

Catechol as a photographic developer behaves in some ways as a typical singly charged agent¹ and is presumably active in the form of the univalent ion. The way in which the rate of development depends upon the pH cannot be explained, however, simply on the basis of a change in the concentration of the univalent ion. Thus, Bürki and Ostwalt² found that the rate of development increased nearly fivefold when the pH was increased from 9.20 to 10.37. The pK_1 value for catechol in a solution of the salt concentration

used by them is about 9.20,³ so that complete primary ionization of the catechol would result in merely doubling the concentration of the univalent ion over its value at pH 9.2. Accordingly, the bivalent ion also must be active. The pK_2 value for the second ionization of catechol has not been determined, and must be higher than 12. Joslyn and Branch have obtained evidence that the bivalent ion is an active absorber of oxygen in the oxygen oxidation of catechol at pH above 10, and have estimated from their kinetic data that the pK_2 value is about 13.

Kinetic experiments on development, carried out under simplified conditions, previously described,⁴ indicate that the bivalent ion of catechol is active in the later stages of development even at a pH as low as 7. The catechol was used in phosphate buffered solution and in the absence of sulfite. Development was carried out in the absence of oxygen.

Figure 1 shows the dependence of development rate upon catechol concentration at pH 7.70. The upper curve, R, refers to development rates determined on the basis of the maximum rate of increase of density per unit time, and hence to development well beyond the induction-period. The lower curve, $1/t$, refers to rates which were determined as the reciprocal of the time required to obtain a density of 0.10, or approximately 3% of the maximum density obtainable. These are largely, although not purely, induction-period rates. The slope of the R plot is 0.57, that of the $1/t$ plot is 0.73, indicating adsorption of the developing agent prior to reaction.⁴

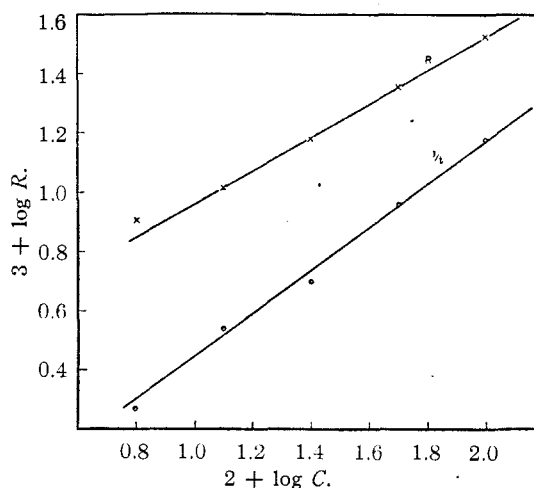


Fig. 1.—Dependence of development rate on catechol concentration at pH 7.70; $\log E = 1.90$.

Figure 2 shows the dependence of development rate upon the pH for constant catechol concentration. The slope of the R plot is 1.01, that of the $1/t$ plot is 0.82. If the univalent ion only were in-

(3) M. A. Joslyn and G. E. K. Branch, *THIS JOURNAL*, **57**, 1779 (1935).

(4) T. H. James, *J. Phys. Chem.*, **44**, 42 (1940).

(1) T. H. James, *J. Franklin Inst.*, **240**, 15 (1945).

(2) F. Bürki and U. Ostwalt, *Helv. Chim. Acta*, **22**, 30 (1939).

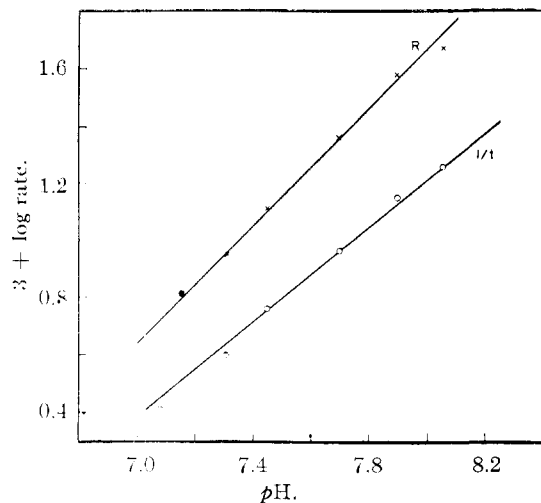


Fig. 2.—Dependence of development rate on pH at constant catechol concentration ($0.5 M$); $\log E = 1.90$.

involved, the same dependence should be obtained whether the concentration of that ion were changed by altering the total catechol concentration at constant pH or the pH at constant total concentration. If only the bivalent ion were involved, the slope of the curve representing log rate as a function of pH should be approximately twice that of the curve representing log rate as a function of catechol concentration for constant pH . Actually, the slope of the $1/t$ curve in Fig. 2 is only slightly greater than that of the corresponding curve in Fig. 1, indicating that the univalent ion is primarily responsible for development in the induction-period region. Moreover, since the $1/t$ rates are not purely induction period rates but are combined to some extent with rates beyond the induction period, many of the development centers having passed beyond the induction period at a density of 0.1, it is probable that the univalent ion is almost entirely responsible for development in the induction-period region. The slope of the R curve in Fig. 2 is approaching twice that of the corresponding curve in Fig. 1, indicating that the bivalent ion is primarily responsible for development beyond the induction period, but the univalent ion is still taking some part.

Other properties of the catechol developer fall in line with what might be expected on the basis of this interpretation. The neutral salt effect is somewhat greater than that obtained with purely univalent agents, such as *p*-aminophenol, but not as great as that obtained with purely bivalent agents, such as hydroquinone and ascorbic acid. Phenosafranin accelerates development by catechol (Fig. 3), but not to as great an extent as it accelerates development by hydroquinone. The difference is particularly noticeable when the developer contains no added bromide. Phenosafranin then has only a slight accelerating effect upon development by catechol, whereas the effect

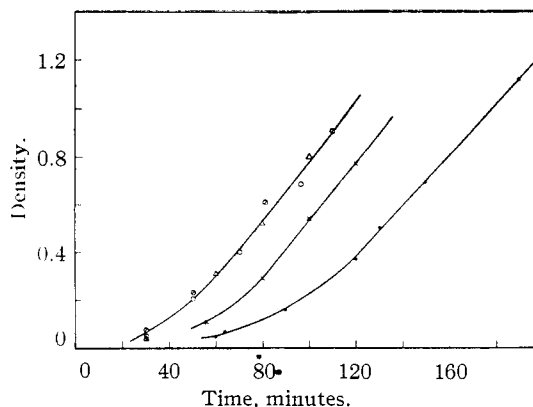


Fig. 3.—Effect of phenosafranin on development by catechol: catechol, $0.05 M$; pH , 7.69; KBr , $0.00033 M$; $\log E = 1.90$: $\bullet-\bullet-$, no addition; $-X-X-$, $0.00002 M$ phenosafranin; $-\Delta-\Delta-$, $0.00004 M$; $-\circ-\circ-$, $0.00008 M$; $-\square-\square-$, $0.0002 M$.

upon development by hydroquinone is already marked (see Table I).

TABLE I

COMPARISON OF EFFECT OF PHENOSAFRANIN UPON RATE OF DEVELOPMENT BY CATECHOL AND BY HYDROQUINONE;

Phenosafranin concn., M	NO ADDED BROMIDE			
	Development by catechol pH 7.69		Development by hydroquinone pH 8.29	
	Time to reach $0.1D_{\infty}$, min.	R	Time to reach $0.1D_{\infty}$, min.	R
None	23	0.021	20	0.067
0.00004	17	.023	7	.144

If 13 is accepted as the pK_2 value of catechol, the concentration of univalent ion at pH 8 will be about 10^5 times that of the bivalent ion. The specific rate of reaction of the bivalent ion, accordingly, must be much greater than that of the univalent ion. In the induction-period region, the charge effect⁵ evidently more than offsets the difference in specific rates, and the univalent ion is responsible for practically all of the reaction in this early stage. Beyond the induction period, the charge effect no longer makes a marked distinction between the singly and doubly charged ions, and the bivalent ion takes over most of the development reaction, just as the bivalent developer may in the action of certain complex developers.⁶

It might be expected that at high pH , where the concentration of bivalent ion would be comparable to that of the univalent ion, the character of the development would change definitely to that of the bivalent ion. At pH 12, for example, the ratio of bivalent ion concentration to univalent ion concentration would be 10^4 times as great as at pH 8. The rate of development, however, increases only as about the square root of the concentration of bivalent ion, and the dependence on the concentration of univalent ion, at least in the

(5) T. H. James, *J. Franklin Inst.*, **240**, 83 (1945).

(6) *Ibid.*, **240**, 327 (1945).

induction-period region, is greater than this. The relative increase, therefore, would be less than 10², and this probably is not enough to cause a shift in the induction-period reaction from the characteristics of a univalent ion reaction to those of a bivalent ion reaction.

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The Molar Refraction of Sulfonyl Chlorides

BY EDWARD F. LANDAU¹

Except for the early work of Nasini,² there is little published information regarding the molar refraction of tetravalent compounds of sulfur. In a previous publication,³ we evaluate the molar refraction of the —SO₂O— group in a series of ethylenesulfonic esters. This value was 9.7 ± 0.2.

In the course of this investigation several liquid aliphatic sulfonyl chlorides were prepared. Their molar refractions were determined and the value of the sulfonyl chloride group compared with two other liquid sulfonyl chlorides. The molar refraction of the sulfonyl chloride group as determined from the five compounds listed, is 15.40 ± 0.07.

4-Quinolinemethanol

BY S. F. MACDONALD

As lepidine undergoes a condensation of the Mannich type with an aldehyde and an amine,¹ 4-quinolinemethanol was prepared in the hope that it would do likewise. Unfortunately, we have been unable to condense it with cotarnine or with formaldehyde and piperidine. Such a condensation would have provided an attractive theory as to the biogenesis of the cinchona alkaloids: a Mannich condensation between 4-quinolinemethanols and one² of the stereoisomeric aldehydes of meroquinine; the latter possibly formed from 6-keto-decahydroisoquinoline, by a photolytic reaction analogous to the conversion of cyclohexanone into hexenal.³

The preparation of quinoline-4-aldehyde⁴ was modified to eliminate difficulties due to bumping and the tedious steam distillation; using acetic acid as solvent we got the same yields with freshly prepared and with year-old selenium dioxide.

Experimental

Quinoline-4-aldehyde (Anhydrous).—A mixture of 40 g. of lepidine, 400 ml. of acetic acid, and 80 ml. of acetic anhydride was stirred at 85–90° and 45 g. of powdered sublimed selenium dioxide added over one and a quarter hours. The mixture was heated one and a half hours longer, cooled and filtered. The filtrate was treated with

TABLE I
MOLAR REFRACTION OF SULFONYL CHLORIDES

Compound	°C. B. p.,	Mm.	<i>n</i> ²⁰ _D	<i>d</i> ²⁰ ₄	<i>M</i> _D ^a (obs.)	<i>M</i> _D -SO ₂ Cl ^b
2-Bromoethanesulfonyl chloride ^c	82	5	1.5227	1.894	33.44	15.31
2-Chloroethanesulfonyl chloride	68	5	1.4920	1.555	30.72	15.52
Ethylenesulfonyl chloride	52–56	10	1.4686	1.393	25.31	15.45
Benzenesulfonyl chloride			1.5505 ^d	1.378 ^e	40.73	15.35
<i>i</i> -Butylenesulfonyl chloride ^d	68–70	8	1.4779	1.2704	34.43	15.36

^a "Landolt-Börnstein Tabellen," Vol. II, p. 986, Bruel values. ^b Evaluated by difference. ^c Marvel, Bailey and Sparberg, *THIS JOURNAL*, **49**, 1833 (1927). ^d Suter, Malkemus and Archer, *ibid.*, **63**, 1596 (1941). ^e At 23°.

Experimental

Ethylenesulfonyl Chloride.—Powdered phosphorus pentachloride (22 g.) was added in small portions to a rapidly agitated suspension of 12.5 g. ammonium ethylenesulfonate³ in 100 ml. of chloroform. The temperature of this suspension was maintained at 30–40° for two hours. The chloroform was removed by distillation and the residue dissolved in 50 ml. of ether. After three washings with 50-ml. portions of water, the ethereal solution was dried and distilled. Two fractions were obtained. Fraction I, 4 g.; b. p. 52–56° (1 mm.); *n*²⁰_D 1.4686; *d*²⁰₄ 1.393.

Anal. Calcd. for C₂H₃O₂ClS: S, 25.34; sapon. equiv., 63.3. Found: S, 25.62, 25.51; sapon. equiv., 64.5. Fraction II, 4 g., b. p. 70–72° (5 mm.); *n*²⁰_D 1.4740; *d*²⁰₄ 1.439; sapon. equiv., 67.7. This fraction was possibly a polymeric vinyl sulfonyl chloride.

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(1) Present address: Celanese Corporation of America, Newark, New Jersey.

(2) Nasini, *Ber.*, **15**, 2844 (1882).

(3) Whitmore and Landau, *THIS JOURNAL*, **68**, 1797 (1946).

70 ml. of concentrated hydrochloric acid, allowed to stand at 10° overnight and filtered. The aldehyde in the filtrate was isolated by steam-distilling off the excess acetic acid, neutralizing the remainder with sodium hydroxide then magnesium oxide, and distilling the aldehyde over in steam. The hydrochloric acid precipitate, containing most of the aldehyde, was dissolved in water, filtered, treated with excess sodium hydroxide and the aldehyde filtered off. The two lots of aldehyde were combined, dehydrated by heating *in vacuo* in the distilling flask and distilled *in vacuo*, collecting at 98–108° (ca. 0.1 mm.); yield 50–60%, m. p. 48–49° (uncor.).

Quinoline-4-methanol.—A mixture of 30 g. of quinoline-4-aldehyde, 200 ml. of anhydrous *i*-propyl alcohol, and 6.3 g. of aluminum *i*-propylate was distilled slowly through a Widmer column until the temperature at the top of the column rose to 82°, the volume being kept constant by the occasional addition of *i*-propyl alcohol. Thirty ml. of water was then added to the contents of the flask, and water and *i*-propyl alcohol removed by heating *in vacuo*.

(1) Heou-Feo, *Bull. soc. chim.*, [5] **2**, 96 (1935).

(2) King, *J. Chem. Soc.*, 523 (1946).

(3) Ciamician and Silber, *Ber.*, **41**, 1071 (1908).

(4) Kwartler and Lindwall, *THIS JOURNAL*, **59**, 524 (1937); Kajan, *ibid.*, **63**, 2654 (1941).