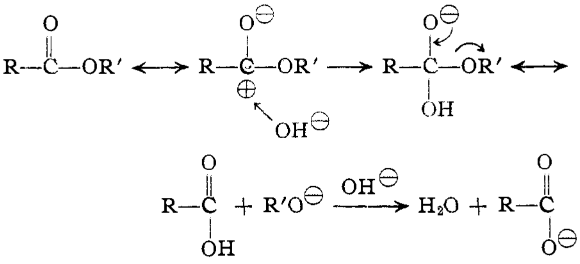
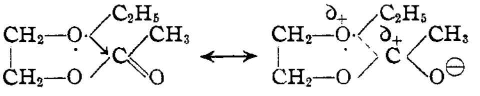
That 2-ethoxyethanol-1 acetate should deviate from this regularity indicates that a factor, not present in the other members of the series, has been introduced and which affects the ease of the reaction.

An explanation for this discrepancy can be found in the commonly accepted mechanism for the basic hydrolysis of esters.



Now, in the case of the ether ester, the ether-oxygen atom can partially donate its unpaired electrons to the carbon atom at which the attack is to be made by the hydroxyl ion, thereby forming a "quasi" five-membered ring



Ingold and Nathan[5] have found that, in the case of para-substituted benzoic esters, groups which donate electrons to the site of attack will increase the energy of activation of the reaction. It would appear that this effect is operating in the case of the "quasi" five-membered ring, while the existence of steric hindrance due to the ethoxy group cannot be excluded. In addition to a raising of the energy of activation, one would expect a slowing down of the reaction, but this cannot be shown from the above data, although there is no reason for suspecting that this has not been the case.

It is of interest to compare these conclusions with those drawn by T. I. Crowell and L. P. Hammett from their work on the reaction of the thiosulfate ion on alkyl bromides.[6] The decrease in rate of reaction in going from ethyl to isopropyl bromide is attributed to an increase in the activation energy of the latter reaction, whilst in going from ethyl to propyl bromide the decreased rate is attributed to a decrease in the entropy of activation. It would seem that our series would conform with this latter case, since the increase in rates in the series must, it seems, be due to increases in entropy of activation, with an especially large jump from the ethyl to the ether-ester.

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(5) Ingold and Nathan, *J. Chem. Soc.*, 222 (1936).

(6) T. I. Crowell and L. P. Hammett, THIS JOURNAL, **70**, 3444 1948).

The σ-Constants of the Cyano Group

BY JOHN D. ROBERTS* AND ELIZABETH A. MCELHILL

Despite the importance of the cyano group as a substituent group of organic compounds, relatively few data are available for the quantitative evaluation of its electrical effect on organic reactions. Thus, while Hammett's compilation[1] includes a value (based on a single reaction) for the σ-(substituent) constant of the *m*-cyano group, none is given which applies to compounds other than anilines or phenols for the *p*-cyano group.

As part of another investigation we have had occasion to determine the influence of the *m*- and *p*-cyano groups on the reactivity of benzoic acid and, hence, the corresponding σ-constants. The reactions and procedures have been described previously in detail.[2] The apparent ionization constants at 25° in 50% water–50% ethyl alcohol (by volume) of *m*- and *p*-cyanobenzoic acids[3] were 1.41×10^{-5} and 2.00×10^{-5}, respectively, while the corresponding rate constants (k_2) for the acids with diphenyldiazomethane at 30° in absolute ethyl alcohol were 4.55 and 4.22 l./mole-min. The σ-constants calculated from all of the data now available are given in Table I. The average value of σ for the *p*-cyano group is +0.656 with a median deviation, *r*, of 0.034. The corresponding values for the *m*-cyano group are +0.608 and 0.054, respectively.

TABLE I

σ-CONSTANTS OF CYANO GROUP

Reaction	Log k_0	ρ	σ-*para*	σ-*meta*
Phenylate ions with oxiranes, 98% ethyl alcohol, 70.4°[a]	−4.254	−0.946	......[b]	+0.678
Ionization of benzoic acids, water, 25°[a]	−4.203	+1.000	+0.651[c]	+ .520[c]
Ionization of benzoic acids, 50% ethyl alcohol, 25°[d]	−5.71	+1.464	+ .695	+ .590
Benzoic acids with diphenyldiazomethane, 100% ethyl alcohol, 30°[d]	+0.041	+0.937	+ .622	+ .645

[a] Ref. 1. [b] The value obtained from this reaction is only applicable to anilines and phenols. [c] Calculated from the data of Kilpatrick and Eanes, THIS JOURNAL, **65**, 589 (1943). [d] Ref. 2.

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* Harvard University. National Research Fellow 1945–1946.

(1) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1940, Chap. VII.

(2) Roberts, McElhill and Armstrong, THIS JOURNAL, **71**, 2923 (1949).

(3) Kindly furnished by Dr. J. T. Clarke.

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Preparation of *d,l*-Cysteine Hydrochloride

BY RICHARD B. TURNER* AND DOROTHY M. VOITLE

Although various derivatives of *d,l*-cysteine are well known, preparation of the hydrochloride of

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the free amino acid in pure form has not been recorded in the literature.[1] In connection with studies in which S^{35} was employed we had occasion to synthesize pure *d,l*-cysteine hydrochloride and wish to report our data at this time.

An optically inactive mixture of *d,l*-cystine and *meso*-cystine[2] was prepared from elementary sulfur by way of benzylmercaptan, benzylthiomethyl chloride, benzylthiomethylphthalimidomalonic ester and S-benzylcysteine by Seligman's[3] modification of the procedure of Wood and du Vigneaud.[4] Reduction of the mixed product with tin and hydrochloric acid afforded *d,l*-cysteine hydrochloride, m. p. 140–141.5° (dec.) in 62% yield. The sulfhydryl content of the product as determined by iodine titration was 98.7% of the theoretical value.

Experimental[5]

d,l-**Cysteine Hydrochloride.**—Optically inactive cystine (418 mg.) was dissolved in 5 ml. of 4.0 *N* hydrochloric acid; 400 mg. of granulated tin was added, and the reaction mixture was allowed to stand at room temperature in an atmosphere of nitrogen. At the end of four hours the tin had dissolved, and the solution was evaporated to dryness under reduced pressure to remove excess hydrochloric acid. The residue was dissolved in water, and the tin removed by saturation with hydrogen sulfide followed by filtration. The filtrate was then concentrated to dryness in vacuum. The crude product was finally washed with ethyl acetate, which removed a small amount of oil, and crystallized from absolute ethanol-ether; yield 340 mg. (62%), m. p. 140–141.5° (dec.). An additional 60 mg. of less pure material, m. p. 137–140° (dec.), was obtained from the mother liquor. All operations were conducted under nitrogen.

Anal. Calcd. for $C_3H_7O_2NS{\cdot}HCl$: C, 22.86; H, 5.11; N, 8.89; S, 20.34; Cl, 22.50. Found: C, 23.00; H, 5.20; N, 8.88; S, 20.66; Cl, 22.56.

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[1] Crude, uncharacterized material has been obtained by Schöberl and Wagner, *Naturwissenschaften*, **34**, 189 (1947), and presumably also by Farlow, U. S. Patent 2,406,362 (1946).

[2] Loring and du Vigneaud, *J. Biol. Chem.*, **102**, 287 (1933).

[3] Seligman, Rutenberg and Banks, *J. Clinical Investigation*, **22**, 275 (1943).

[4] Wood and du Vigneaud, *J. Biol. Chem.*, **131**, 276 (1939).

[5] Microanalyses were performed by Mr. S. M. Nagy of M. I. T.

NEW COMPOUNDS

N,N'-Bis-(trichloromethylmethylol)-melamine

12.6 g. (0.1 mole) of pure melamine[1] was added to a stirred solution of 132 g. (0.8 mole) of chloral hydrate in 125 cc. of water at 70–80°. The melamine was completely dissolved within two minutes and a granular solid began to precipitate. After five minutes heating the suspension was cooled, the product filtered off and washed well with water. It weighed 35 g. (83% yield). On larger scale runs yields were usually 90% of theoretical. *Anal.* Calcd. for $C_3H_6N_6{\cdot}2C_2HOCl_3$: N, 19.95; Cl, 50.6. Found: N, 19.9, 20.2; Cl, 50.5, 50.7.

When heated on a spatula the substance did not melt but evolved chloral. It did not react with boiling formalin. It was stable to dilute sodium hydroxide at room temperature but hydrolyzed rapidly on the steam-bath, liberating chloroform; pure melamine crystallized as the solution cooled.

We have observed that the reaction of chloral with melamine–formaldehyde mixtures or with water soluble methylolmelamines results in the formation of gels; this is attributed to the hydrolysis of chloral which lowers the reaction mixture to *p*H 4.

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[1] Salley and Gray, THIS JOURNAL, **70**, 2650 (1948).

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COMMUNICATIONS TO THE EDITOR

SIMULTANEOUS VICINAL DICHLORINATION

Sir:

Iodine trichloride, postulated as the reagent when iodine is a carrier in direct chlorination,[1] has been neglected as a chlorinating agent. Crepaz[2] obtained *p*-chloroacetanilide when acetanilide was treated with $KICl_4$. Spring and Winssinger[3] heated sulfonic acids with iodine trichloride and obtained various products. Thus ethanesulfonic acid with excess reagent heated to 150° for seven hours produced hexachloroethane and chlorosulfonic acid, but with a smaller amount of reagent apparently 1,2-dichloroethanesulfonic acid was produced. On the other hand, 1-propanesulfonic acid yielded 1,1,1-trichloropropane and chlorosulfonic acid with excess iodine trichloride. The latter case suggests a normal ionic substitution mechanism, but the former is more difficult to interpret. Ingold and Ingold[4] suggest that iodine trichloride acts as a chlorinating agent by dissociating to iodine monochloride and two active chlorine atoms

$$ICl_3 \rightleftarrows ICl + 2Cl$$

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[1] Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 174.

[2] Crepaz, *Atti ist. veneto sci.*, **94**, 555 (1934–1935); *C. A.*, **31**, 6209 (1937).

[3] Spring and Winssinger, *Ber.*, **15**, 445 (1882); **16**, 326 (1883).

[4] Ingold and Ingold, *J. Chem. Soc.*, 1314 (1926).