Notes

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.

$$\begin{array}{c} O & O^{\ominus} & O^{\ominus} \\ R-C-OR' \longleftrightarrow R-C-OR' \longrightarrow R-C-OR' \longleftrightarrow \\ & OH^{\ominus} & OH \\ & OH^{\ominus} & OH \\ & R-C & H_{2}O + R-C \\ & OH^{\ominus} & OH \\ & OH \\ & OH \\ & OH \\ \end{array}$$

Now, in the case of the ether ester, the etheroxygen 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 Nathan⁵ 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.

DEPARTMENT OF CHEMISTRY

HARVARD UNIVERSITY CAMBRIDGE, MASS. RECEIVED SEPTEMBER 6, 1949

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 compilation¹ 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 mand 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 acids³ 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./molemin. 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 +0.656with a median deviation, r, of 0.034. The corresponding values for the *m*-cyano group are +0.608and 0.054, respectively.

Table I

σ -Constants of Cyano Group

0-00031	THIS OF C	THE OF	OUF	
Reaction	Log ko	ρ	σ-para	o-meta
Phenylate ions with oxi	-			
ranes, 98% ethyl alco	-			
hol, 70.4° ^a	-4.254	-0.946	. ^b	+0.678
lonization of benzoic				
acids, water, 25°a	-4.203	+1.000	$+0.651^{\circ}$	+ .520°
lonization of benzoic ac	ids, 50%			
ethyl alcohol, 25° ^d	-5.71	+1.464	+ .695	+ ,590
Benzoic acids with di	phenyl-			
diazomethane, 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.

* 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.

DEPARTMENT OF CHEMISTRY

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

CAMBRIDGE 39, MASSACHUSETTS RECEIVED JUNE 25, 1949

Preparation of d,l-Cysteine Hydrochloride

BY RICHARD B. TURNER* AND DOROTHY M. VOITLE

Although various derivatives of d_i -cysteine are well known, preparation of the hydrochloride of

* Harvard University Ph.D. 1942.

⁽⁵⁾ Ingold and Nathan, J. Chem. Soc., 222 (1986).

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