

This dissociation constant is comparable with that of sulfuric acid, and therefore places azido-dithiocarbonic acid in the class of moderately strong acids.

The data obtained by potentiometric titration of the acid are presented graphically in Fig. 2.

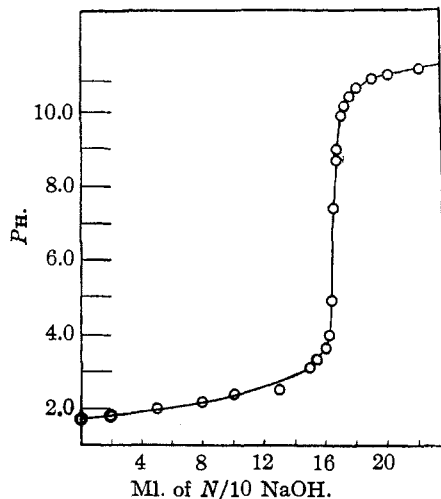


Fig. 2.—Potentiometric titration of azido-dithiocarbonic acid in aqueous solutions.

A sample of the free acid (0.1930 g.) was dissolved in 100 ml. of distilled water, and was titrated with 0.1 *N* sodium hydroxide. The vertical portion of the curve, representing equivalence of acid and base, lies between the *PH* values 3.5 and 9.5, and is therefore in close agreement with the corre-

sponding portion of the curve for sulfuric acid.<sup>12</sup> Cryoscopic data of more concentrated aqueous solutions of the acid are given in Table III.

TABLE III  
CRYOSCOPIC DATA FOR CONCENTRATED SOLUTIONS OF HSCSN<sub>3</sub>

$\Phi$	$\Delta$	Mol. wt.	$\alpha$
21,450	0.119	87.03	0.3695
14,950	.161	91.21	.3085
10,840	.217	95.20	.2520
8,756	.260	97.57	.2218

### Summary

The electrical conductance of azido-dithiocarbonic acid, HSCSN<sub>3</sub>, a halogenoid hydracid, in aqueous solution has been determined. These measurements place the compound in the class of the moderately strong acids. In the family of halogen and halogenoid hydracids, azido-dithiocarbonic acid is therefore to be placed above hydrofluoric, hydrocyanic and hydronitric acids and below hydrochloric, hydrobromic, hydriodic and (probably) thiocyanic acids. This conclusion has been confirmed by potentiometric titration of the azido acid which shows it to be comparable in strength with sulfuric acid, and also by cryoscopic determinations. The equivalent conductivity of the azido-dithiocarbonate ion SCSN<sub>3</sub>, a halogenoid ion, has been established as 41.7 at 25°.

(12) Davis, Oakes and Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923).  
ITHACA, N. Y. RECEIVED MARCH 8, 1934

## NOTE

### Catalytic Decomposition of Lead Tetraphenyl

By M. KOTON

Dull and Simons<sup>1</sup> have described the thermal decomposition of lead tetraphenyl which has also been studied in our laboratory.<sup>2</sup> The above authors state that at 252° the decomposition proceeds without the addition of catalyst. We, however, consider this (and it has been confirmed later on by experiments) to be a special case of the catalytic decomposition of lead tetraphenyl we are studying, in which case the metallic lead separated during the process acts as catalyst. With addition of lead the reaction proceeds at much lower temperatures.

(1) Dull and Simons, *THIS JOURNAL*, **55**, 4328 (1933).  
(2) Koton, *Ber.*, **66**, 1213 (1933).

Experiments have been carried out in small sealed glass tubes (5 cm. length) heated in a metallic bath with Wood's alloy. The temperature was allowed to vary in the range of about  $\pm 1-2^\circ$ .

The lead tetraphenyl used in these experiments had a melting point of 223–225°. The metallic lead had been obtained by reducing lead oxide in a stream of hydrogen at a temperature of 150–180°.

In our experiments the decomposition of lead tetraphenyl began at higher temperatures compared with those of Dull and Simons, which possibly may be explained by the use of different experimental conditions.

In Run 6 newly prepared metallic lead was used which proved to be much more active than that used after standing during three weeks, as seen from Runs 4 and 5.

No.	Ph <sub>4</sub> Pb, g.	Pb, g.	t, °C.	Time, hrs.	Lead, g.	Yield of diphenyl	% of decomp.	Remain. Ph <sub>4</sub> Pb
1	1	...	255°	1	0.011	Trace	2.7	0.94
2	1	...	255°	1	Trace	None	...	.98
3	1	...	255°	2	0.0277	0.03	6.9	.92
4	1	1	245°	1	.0310	.02	7.72	.91
5	1	1	250°	1	.0580	.06	17.46	.80
6	1	1	255°	1	.2626	.38	65.48	.33

The experiment being over, the tube was opened,

the diphenyl extracted with ether and after removal of the latter recrystallized from alcohol. The melting point was in all cases 69–70°.

The remaining lead tetraphenyl was extracted with a mixture of benzene and xylene. After having been washed with ether, lead was determined by usual methods.

LENINGRAD, U. S. S. R.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Polarity and Alcoholysis of 1,3-Diketones and $\beta$ -Keto Esters

BY LELAND J. BECKHAM AND HOMER ADKINS

The experimental findings with respect to the cleavage by alcohol of a number of compounds of the type  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}'}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}''$  have been presented in

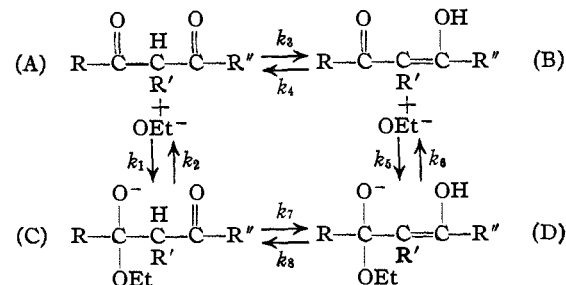
a series of papers.<sup>1,2,3,4,5</sup> It is now possible to rationalize many of these findings upon the basis of the polarization (I effects) and polarizability (T effects) of R, R', R'', and R''', due consideration being given to the number and position of the substituents and to the conditions of reaction. The discussion in this paper is based upon the ideas developed by Ingold, Robinson, Watson, Shoppee, Lapworth, Kon, Linstead, Farmer and others.<sup>6</sup> The terminology adopted is that originally due to Ingold.

The alcoholysis of the 1,3-diketones or the  $\beta$ -keto esters may involve the cleavage of the dicarbonyl compounds, or of the corresponding enols which are more or less chelated. Therefore it is necessary to distinguish between the effect of substituents upon the two types of cleavage as well as upon the extent and position of enolization.

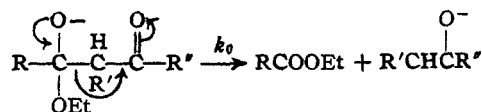
In the ensuing discussion it will be necessary to refer to the three distinctly different conditions under which the experimental results were obtained, *i. e.*, "basic alcoholysis" which occurred in the presence of a considerable quantity of sodium

ethoxide at 60°; "acid alcoholysis" which took place at 60° in the presence of considerable quantities of hydrogen chloride;<sup>1</sup> and "high temperature alcoholysis" which occurred at 150–250° in the presence of traces of water or aluminum ethoxide.<sup>4</sup>

Mechanisms for the cleavage and the competitive enolization of a diketone may be outlined as follows.<sup>7</sup> It is suggested that A, B, C and D occur in basic solutions.<sup>8</sup>



(C) is presumed to be the compound which undergoes cleavage, *i. e.*,



In the presence of acid the following equilibria are established

(7) Cf. Bradley and Robinson, *J. Chem. Soc.*, 129, 2359 (1926).

(8) Compounds B and D as here employed are intended to cover not only the enol form shown but also the corresponding ions and sodium salts, which are present in basic solution. Addition is assumed to take place in every case on the unenolized side of the diketone and is consequently more or less independent of the condition at the other end of the molecule. The fact that alcohol does not add to ketones to any considerable extent indicates that the addition product D is present in much lower concentrations than B (including of course ion and sodium salt). A and C are present in small concentration as would be expected from the concentration of D and the high tendency to enolize in the presence of NaOEt. Consequently the species B may be taken as the predominant species, equal approximately to the total concentration of all forms present.

(1) Adkins, Kutz and Coffman, *This Journal*, 52, 3213 (1930).

(2) Kutz and Adkins, *ibid.*, 52, 4036 (1930).

(3) Kutz and Adkins, *ibid.*, 52, 4391 (1930).

(4) Connor and Adkins, *ibid.*, 54, 3420 (1932).

(5) Isbell, Wojcik and Adkins, *ibid.*, 54, 3678 (1932).

(6) (a) Ingold and Ingold, *J. Chem. Soc.*, 2359 (1931); (b) Ingold, *ibid.*, 1120 (1933); (c) Watson and Yates, *ibid.*, 220 (1933); (d) Shoppee, *ibid.*, 968 (1930); (e) *ibid.*, 1117 (1933); (f) Robinson, *ibid.*, 1114 (1933); (g) "Outline of an Electrochemical Theory of the Course of Organic Reactions," The Institute of Chemistry, Great Britain and Ireland, London, 1932.