the very marked change in the distribution of intensity in this region upon melting (Fig. 2) it seems more reasonable to interpret this as a lattice mode, possibly involving rotation of the $N_2H_5^+$ ion as a rigid unit.

Comparison with the Raman Spectrum.—Although the available Raman data on N_2H_5Cl and N_2D_5Cl refer to aqueous solution, it is nevertheless interesting to compare the data as is done in Table II.

Although the agreement between the infrared and Raman frequencies is not complete, it is perhaps as close as may be reasonably expected in view of the difference in the physical states. Aside from the hydrogen stretching region, the largest differences occur between 1246 and 1274 and between 1500 and 1533.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Rates of Ionization of Pseudo Acids.[1] IV. Relation between Rates and Equilibria

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If the logarithms of the rate constants for ionization of pseudo acids are plotted against the logarithms of the corresponding equilibrium constants, the best straight line divides the compounds into those with positive rate deviations and those with negative deviations. The greater the ability of a substituent to absorb the negative charge generated in the carbanion, the greater the negative deviation. As electron absorbers $NO_2 > CO > CN \geq SO_2$. Compounds having the latter two groups as activators show positive deviations. Thus, nitriles and sulfones are characterized by high rates of ionization for a given acid strength and hence high rates of recombination of their carbanions with a proton. This latter factor causes the rate of bromination of nitriles and sulfones to be dependent on the hydrogen ion and bromine concentrations in contrast to nitro and carbonyl compounds. Substitution of a second electronegative group on a monosubstituted compound makes the rate deviation more positive. This is apparently because a second substituent increases the electronegativitity of the central carbon atom to the point where it controls a relatively greater share of the anionic charge. The common activating groups are arranged in the following order (for equilibria, not rates) $NO_2 > CO > SO_2 > COOH > COOR > CN \sim CONH_2 >$ halogen. This order differs from that obtained from hydroxyl acids. There is shown to be no sharp division between normal and pseudo acids and bases (or primary and secondary). There is instead a gradual transition from one to the other.

In a continuation of our studies of pseudo acids we present in this paper some new data on the rates of ionization in water and the acid ionization constants of some substituted nitro and cyano compounds. We have also accumulated all of the available data on rates and equilibria for the simple carbon–hydrogen acids. The standard reaction is

$$HA + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} A^- + H_3O^+ \qquad (1)$$

where k_1 and $K_a = k_1/k_2$ can generally both be measured. From these k_2, the rate constant for ion recombination, can be calculated.

Experimental

Materials.—1-Chloronitroethane was a sample donated by the Commercial Solvents Corporation. It was purified by dissolving in alkali, extracting with ether and acidifying the aqueous phase with hydroxylamine hydrochloride.[3] The nitro compound thus obtained was fractionated and the product boiling at 37–38° at 20 mm. was used; $n^{25}D$ 1.4235. Hurdis and Smythe[4] report $n^{20}D$ 1.4224.

Ethyl nitroacetate was made according to the literature,[5] b.p. 65° at 2 mm., $n^{25}D$ 1.4229. Ethyl cyanoacetate was made according to "Organic Syntheses," b.p. 198°, $n^{20}D$ 1.4176. Ethyl monobromcyanoacetate was made according to the literature,[6] b.p. 135° at 40 mm.

A sample of malononitrile obtained from the Schwarz Laboratories was recrystallized twice from water, m.p. 31° (literature value 32.1°). Monobromomalononitrile was made according to Hesse,[7] m.p. 62° (literature 65°).

Potassium dinitromethane was made by the procedure of Duden.[8] The product was recrystallized from water. Since the free acid is unstable, the salt was acidified with an equivalent amount of acid just before use.

A sample of nitroacetone was kindly supplied by Dr. May Nilson of this Laboratory, m.p. 46–48° (literature values of 46.5 and 49° have been reported). The compound was stored under ether.

Methods.—The rates of ionization were determined by measuring the rates of bromination using the conductometric method previously described.[1] An open neck conductance cell was used so that mixing of reagents could be done in the cell. An excess of bromine was used and the conductance data plotted as for a first-order reaction. The slowly reacting 1-chloronitroethane was also treated as a zero-order reaction using low concentrations of bromine. The equilibrium resistance was determined sometimes directly on the reaction mixture and sometimes from synthetic mixtures of hydrobromic acid corresponding to the final concentration. The same results were obtained by the two methods.

The conductance method was checked by direct titration of unreacted bromine in the case of 1-chloronitroethane. For ethyl nitroacetate a check was made by adding allyl alcohol followed by potassium iodide so that the amount of bromine reacted could be determined with standard thiosulfate.

Ethyl nitroacetate, ethyl cyanoacetate, nitroaceton, dinitromethane and malononitrile used up two moles of bromine per mole of pseudo acid. Since good first-order kinetics were obtained up to 80% reaction, it was assumed that the second stage of bromination was much faster than the first. This was checked in the case of ethyl cyanoacetate and malononitrile by making the monobrominated derivative and measuring its rate of bromination (see Table III). That the above assumption is not always true has been

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[1] For previous papers in this series see THIS JOURNAL, **72**, 1692, 3594 (1950).

[2] Based on a portion of the Ph.D. dissertation of Robert L. Dillon, Northwestern University, 1951.

[3] This procedure was suggested by Prof. Nathan Kornblum.

[4] E. C. Hurdis and C. P. Smyth, THIS JOURNAL, **64**, 2829 (1942).

[5] Rodionov, Mochinskaya and Belikov, *Zhur. Obschei Khim.*, **18**, 917 (1948).

[6] G. Errera and F. Perciabosco, *Ber.*, **33**, 2976 (1900).

[7] B. C. Hesse, *Am. Chem. J.*, **18**, 728 (1896).

[8] P. Duden, *Ber.*, **26**, 3003 (1893).

shown by Bell.[9] The rates of bromination have been divided by two to get the rate of ionization in cases where dibromination occurred.

It was observed that 1-chloronitroethane in aqueous solution (no added bromine) liberated chloride ions. This was studied as a function of time by Volhard titration and found to obey a first-order law. The rate constant at 34.9° was found to be 4.8×10^{-5}, This is just half the rate of bromination. It would be attractive to assume the rate of ionization to be rate determining for the decomposition which gives chloride ions, just as the rate of ionization of nitroethane in dilute aqueous acid is rate determining for its decomposition into hydroxamic acid.[10] This would require that 1-chloronitroethane undergo dibromination so that its rate of ionization is one-half its rate of bromination. However, only one mole of bromine was consumed after three weeks time.

The products of decomposition of 1-chloronitroethane were not determined. However, this reaction has no influence on the rate of bromination, since in the presence of bromine the decomposition does not occur. Thus rates of bromination calculated from resistance measurements and from direct titration of bromine agree, showing that chloride ion cannot be liberated during bromination.

Of all the pseudo acids studied in this work only malononitrile gave a rate dependent on the bromine or hydrogen ion concentration. Some of the pertinent results are shown in Table I. By using high bromine concentrations and no initially added acid it was possible to get some good first order kinetics with a rate constant independent of the bromine concentration (see runs E15, 16, 18 and 19 in Table I). Widequist[11] has studied the rate of bromination of methylmalononitrile in 0.5 *N* acid and found the rate to be first order in the bromine concentration as well as in the nitrile.

TABLE I

RATE OF BROMINATION OF MALONONITRILE AT 0°

Run no.	Malononitrile, mole/l.	Bromine, mole/l.	HBr initial, mole/l.	k_1, min.$^{-1}$
E12	0.00125	0.00251	0.00137	0.072
E13	.00125	.00251	.00274	.041
E14	.00232	.00464	0	.108
E15	.00193	.00570	0	.126
E16	.00193	.0110	0	.126
E18	.00308	.0231	0	.130
E19	.00308	.0060	0	.123
E33	.00122	.0059	.0089	.038
E34	.00122	.0118	.0089	.067

Extrapolation of resistances back to zero time gave no indication of significant amounts of enol form for any of the compounds studied. That is, for fresh solutions, there was no instantaneous take-up of bromine.

Ionization Constants.—A Beckman model G *p*H meter was used with a No. 1190-E glass electrode. Calibration was by means of the borate buffers recommended by Manov.[12] Ionization constants at 25° were calculated from the *p*H of solutions of the pseudo acid partially neutralized with carbonate-free sodium hydroxide. Since some form of cleavage or hydrolysis occurred for each of the pseudo acids investigated, *p*H readings were taken as a function of time and extrapolated back to zero time. Decomposition was so marked in the case of 1-chloronitroethane and ethyl cyanoacetate that no reliable values of the ionization constants could be obtained. Upper limits were obtained by measuring the *p*H of unbuffered solutions after times sufficient to substantially reach equilibrium as judged from the rates of ionization. The same procedure was followed for bromomalononitrile and ethyl bromocyanoacetate. Table II shows the data on ionization constants.

TABLE II

IONIZATION CONSTANTS OF SOME PSEUDO ACIDS AT 25°

$$HA + H_2O = H_3O^+ + A^-$$

Compound	K_a
Ethyl nitroacetate	$1.52 \pm 0.02 \times 10^{-6}$
Nitroacetone	$8.0 \pm 0.5 \times 10^{-6}$
Malononitrile	$6.5 \pm 0.5 \times 10^{-12}$
1-Chloronitroethane	$<10^{-7}$
Ethyl bromocyanoacetate	$\sim10^{-6}$
Bromomalononitrile	$\sim10^{-5}$
Ethyl cyanoacetate	$<10^{-9}$

Discussion

Table III shows the results obtained in this work.

TABLE III

RATES OF IONIZATION OF SOME PSEUDO ACIDS

$$HA + H_2O \longrightarrow A^- + H_3O^+$$

Compound	T, °C.	k_1, min.$^{-1a}$	E_a, kcal.	$\Delta S^\ddagger$, e.u.
1-Chloronitroethane	34.9	$1.0 \pm 0.1 \times 10^{-4}$	20	−22
	47.5	$3.7 \pm .1 \times 10^{-4}$		
Ethyl nitroacetate	0.0	$3.20 \pm .05 \times 10^{-2}$	16	−16
	10.0	$9.15 \pm .05 \times 10^{-2}$		
Ethyl cyanoacetate	0.0	$4.25 \pm .05 \times 10^{-3}$	17	−14
	10.0	$1.40 \pm .05 \times 10^{-2}$		
Malononitrile	0.0	$6.03 \pm .05 \times 10^{-2}$	18	− 7
	10.0	$1.75 \pm .05 \times 10^{-1}$		
Nitroacetone	0.0	$1.21 \pm .05 \times 10^{-1}$	19	− 3
	10.0	$3.85 \pm .05 \times 10^{-1}$		
Dinitromethane	0.0	$2.7 \pm .1$		
Ethyl bromocyanoacetate[b]	0.0	~5		
Bromomalononitrile[b]	0.0	>10		

[a] At least six runs on each compound. The average deviations are given. [b] Only one run attempted.

Table IV shows all of the available rate data on the water-catalyzed ionization of pseudo acids of simple structure. In addition acid ionization constants and calculated rates of ion recombination where known are listed. To clarify these data Fig. 1 shows log k_1 plotted against log K_a for all compounds where both quantities are known. Not all of the data has the same accuracy. In particular the ionization constants of the weakest acids could be in error by as much as a factor of ten. A straight line with a slope of 0.60 has been drawn through the points even though it is obvious that there is only a rough correlation between the rate constants and the equilibrium constants. Theoretically there is no reason to expect a single linear relationship over such a wide range of acid strengths. Thus one might well expect the slope to be nearly unity for extremely weak acids and approach zero for very strong acids. However, the line is convenient for discussing compounds with positive and negative rate deviations, that is, with rates of ionization which are relatively greater or less than they should be in terms of the over-all free energy change.

Thus the simple nitro compounds are conspicuously slow in ionizing considering their acid strengths. The trifluoromethyl diketones and the substituted nitro compounds also show negative deviations. Compounds containing two carbonyl

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[9] R. P. Bell, E. Gelles and E. Moller, *Proc. Roy. Soc.* (*London*), **A198**, 300 (1949).

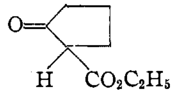
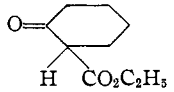
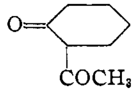
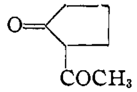
[10] R. Junell, *Arkiv Kemi*, **11B**, 30 (1934).

[11] S. Widequist, *ibid.*, **26A**, 2 (1948).

[12] G. G. Manov, "Symposium on *p*H Measurement, American Society for Testing Materials, Technical Publication No. 73," Philadelphia, Pa., 1946.

TABLE IV

RATE AND EQUILIBRIUM DATA FOR PSEUDO ACIDS AT 25° IN WATER

No.	Compound	K_a[a]	k_1, min.$^{-1}$	k_2, l./mole-min.	References
1	CH_3NO_2	6.1×10^{-11}	2.6×10^{-6}	4.1×10^{4}	13, 14
2	$C_2H_5NO_2$	2.5×10^{-9}	2.2×10^{-6}	9.0×10^{2}	15, 16
3	$CH_3CHClNO_2$	$<10^{-7}$	3.4×10^{-5}	....	...
4	$C_2H_5O_2CCH_2NO_2$	1.5×10^{-6}	3.8×10^{-1}	2.5×10^{5}	...
5	$CH_3COCH_2NO_2$	8.0×10^{-6}	2.2	2.3×10^{5}	...
6	$CH_2(NO_2)_2$	2.7×10^{-4}	50[b]	1.9×10^{5}	17
7	CH_2BrNO_2	....	8×10^{-4}	....	13
8	$CH(NO_2)_3$	Strong	....	....	37
9	CH_3COCH_3	10^{-20}	2.8×10^{-6}	3×10^{12}	18
10	CH_3COCH_2Cl	3×10^{-17}	3.3×10^{-6}	1×10^{11}	18
11	$CH_3COCHCl_2$	10^{-15}	4.4×10^{-5}	4×10^{10}	18
12	$CH_3COCH_2CO_2C_2H_5$	2.1×10^{-11}	7.2×10^{-2}	3.5×10^{9}	19, 20
13	$CH_3COCHC_2H_5CO_2C_2H_5$	2×10^{-13}	4.5×10^{-4}	2.3×10^{9}	21
14	$CH_3COCHBrCO_2C_2H_5$	....	3.6×10^{-1}	....	9
15	$CH_3COCH_2COCH_3$	1.0×10^{-9}	1.0	1.0×10^{9}	9, 20
16	$CH_3COCHCH_3COCH_3$	1.0×10^{-11}	5×10^{-3}	5.0×10^{8}	21, 22
17	$CH_3COCHBrCOCH_3$	1×10^{-7}	1.4	1×10^{7}	9, 22
18	$CH_3COCH_2COC_6H_5$	4×10^{-10}	6.6×10^{-1}	1.6×10^{9}	9, 20
19	$CH_3COCHBrCOC_6H_5$	....	3.3×10^{-1}	....	9
20	$CH_3COCH_2COCF_3$	2×10^{-5}	9.0×10^{-1}	4.5×10^{4}	23
21	$C_6H_5COCH_2COCF_3$	1.5×10^{-7}	5.0×10^{-1}	3.3×10^{6}	23
22	$C_6H_5COCH_2NC_5H_5^+$	3.1×10^{-11}	....	....	24
23		8.0×10^{-7}	6.0×10^{-1}	7.5×10^{5}	23
24		3×10^{-11}	1.4×10^{-1}	5×10^{9}	25
25		3×10^{-12}	5.8×10^{-4}	2×10^{6}	26
26		8.1×10^{-11}	....	....	22
27		1.5×10^{-8}	....	....	22
28	$CH_2(CHO)_2$	1×10^{-5}	....	....	22
29	CH_3COCH_2CHO	1.2×10^{-6}	....	....	27
30	$CH(COCH_3)_3$	1.4×10^{-6}	....	....	28
31	$CH_3COCHCH_3SO_2C_2H_5$	....	1.1×10^{-2}	....	29
32	$CH_3COCH_2CO_2CH_3$	1×10^{-10}	(2.0)[d]	2×10^{10}	22
33	$CH_3SO_2CH_3$	(10^{-23})	2×10^{-10}[c]	....	30
34	$CH_3SO_2CH_2SO_2CH_3$	1×10^{-14}	....	....	22
35	$CH(SO_2CH_3)_3$	Strong	....	....	22
36	$CH_3SO_2CH(COCH_3)_2$	2×10^{-5}	....	....	22
37	CH_3CN	(10^{-25})	4×10^{-12}[c]	....	31
38	$CH_2(CN)_2$	6.5×10^{-12}	9.0×10^{-1}	1.4×10^{11}	...
39	$C_2H_5O_2CCH_2CN$	$<10^{-9}$	7×10^{-2}	....	...
40	$CH(CN)_3$	Strong	....	....	37
41	$CH_3CO_2C_2H_5$	$(10^{-24.5})$	....	....	...
42	$CH_2(CO_2C_2H_5)_2$	5×10^{-14}	1.5×10^{-3}	3×10^{10}	9, 21
43	$CHBr(CO_2C_2H_5)_2$	....	1.8×10^{-2}	....	9
44	$CHC_2H_5(CO_2C_2H_5)_2$	10^{-15}	2×10^{-5}	2×10^{10}	21
45	CH_3CO_2H	(10^{-24})	2×10^{-11}	....	31
46	$CH_2(CO_2H)_2$	....	1.7×10^{-1}[b]	....	32
47	CH_3COCH_2COOH	....	7.8	....	33
48	CH_3CONH_2	(10^{-25})	2×10^{-12}[c]	....	31

[a] This is the gross acid constant uncorrected for enol content. [b] Estimated from data at 0° taking E_a as 18 kcal. [c] Estimated from rate of deuterium exchange catalyzed by hydroxide ion assuming same ratio for k_{H_2O}/k_{OH} as for acetone. [d] Estimated from compounds 16 and 31.

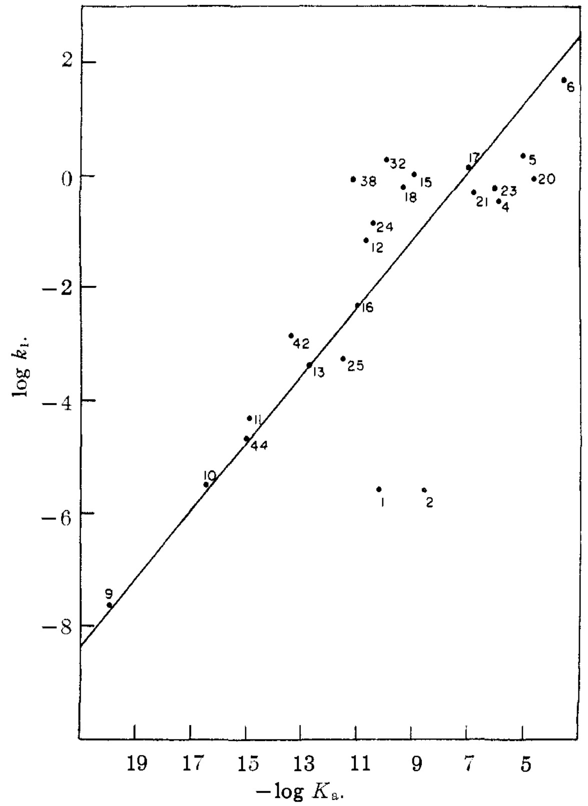


Fig. 1.—Compounds numbered as in Table IV.

or carbethoxy groups have positive deviations. Compounds containing cyano and sulfone groups give the greatest positive deviations. The rate of ionization of a β-disulfone is not known but it would undoubtedly show a large positive deviation (see below).

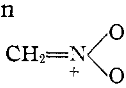
The effect of ring size in the case of the cyclic keto esters is worth mentioning. The five-membered ring is similar to the straight chain analog in showing a positive deviation. The six-membered ring is much slower to ionize as well as being a somewhat weaker acid.

If, instead of log k_1, the log of k_2 had been plotted against log K_a, a plot very similar to Fig. 1 would necessarily be obtained. That is, compounds with a relatively low rate of ionization would have a low rate of ion recombination. Compounds with a relatively high rate of ionization would have a high rate of ion recombination. This latter fact explains why it is that nitriles and sulfones have a rate of bromination dependent on the bromine concentration.[34] Thus, to be independent of the bromine concentration, the rate of combination of the carbanion with bromine

$$A^- + Br_2 \xrightarrow{k_3} ABr + Br^-$$

must be much more rapid than the rate of reversal of reaction (1), that is, recombination of the carbanion with hydrogen ion.

An explanation of the rate deviations in Fig. 1 can readily be given. A strongly electron attracting group such as nitro gives a carbanion in which the negative charge has been almost completely removed from the carbon atom originally holding the acidic hydrogen



$$CH_2{=}\overset{+}{N}\Big\langle{}^{O^-}_{O^-}$$

This removal of charge from the carbon atom slows down the rate at which the carbon atom can again pick up a proton to form the neutral nitro compound. Thus, nitromethane has a higher acid strength than is consistent with its rate of ionization because the carbanion is stabilized by the electronic shift which takes place after ionization. The carbonyl group is less efficient than the nitro group in removing the charge and the cyano and sulfone groups are less efficient still.[35] The efficiency of a carbonyl group can be increased by halogen substitution as in CF_3CO.

The effect of a second unsaturated group is interesting. One might have expected the anion of dinitromethane to be very slow in combining with a proton because the negative charge can now be absorbed by two nitro groups. Actually the rate constant k_2 is greater for dinitromethane than for nitromethane! This must be explained by saying that the second nitro group increases the electronegativity of the central carbon atom to the point where it controls a greater share of the negative charge than it did in the mononitro derivative. The same effect shows up in all the disubstituted compounds to the extent that they show more positive deviations than the monosubstituted derivatives. An alkyl group, on the other hand, when substituted on the central carbon atom makes for more negative deviations. This is attributed to the inductive effect which makes the central atom less electronegative.

Prediction of K_a Values.—From a consideration of Fig. 1 and the known rates of ionization, it would be possible to estimate the ionization constants of weak monosubstituted pseudo acids. Actually only the rates of ionization with hydroxide ion are known for these weak acids. However, the

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(28) L. Birkenbach, K. Kellermann and W. Stein, *Ber.*, **65**, 1072 (1932).

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(32) R. W. West, *J. Chem. Soc.*, **125**, 1287 (1924).

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(35) This is the same order that is observed when comparing the effects of these four groups on the ionization constants of phenols when in the meta and para positions, respectively. F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

TABLE V

SATURATION EFFECT IN POLYSUBSTITUTED ACIDS

	*p*Ka		*p*Ka		*p*Ka		*p*Ka
CH_4	40						
CH_3NO_2	11	CH_3COCH_3	20	$CH_3SO_2CH_3$	23	CH_3CN	25
$CH_2(NO_2)_2$	4	$CH_2(COCH_3)_2$	9	$CH_2(SO_2CH_3)_2$	14	$CH_2(CN)_2$	12
$CH(NO_2)_3$	0	$CH(COCH_3)_3$	6	$CH(SO_2CH_3)_3$	0	$CH(CN)_3$	0

ratio of the rates for water and for hydroxide ion should not change too much in going from acetone to other monosubstituted acids of the same strength and the ratio has been assumed constant. The acid ionization constants obtained in this way have been checked by seeing that the corresponding reverse rate constants, k_2, did not exceed the theoretical limiting value of *ca.* 10^{13} l./mole min. predicted by Onsager's theory[36] for ion recombination. There are reasons why the rate of recombination of two oppositely charged ions could be less than given by this theory, but it is difficult to see how it could be greater. The estimated constants are shown in parentheses in Table IV. The order of effect of the common activating groups on the acidity of acids of the CH_3X type is thus $NO_2 > CO > SO_2 > COOH > COOR > CN \simeq CONH_2 >$ halogen. This is not the same order as would be obtained from a consideration of acids of the HOX type which gives[37] $SO_2 > NO_2 > COOH \simeq CN > CO >$ halogen.

It can be misleading to estimate the ionization constant of a di- or trisubstituted acid from those of the monosubstituted acids. This is illustrated in Table V. Evidently there is a saturation effect which sets in more strongly the greater the electron withdrawing power of the substituting group.

Primary and Secondary Acids and Bases.—Several years ago Lewis and Seaborg[38] suggested that there was a fundamental difference, not of degree but of kind, between primary acids and bases which react with each other instantaneously, and secondary acids and bases which are slow in all their neutralization reactions. Now both the forward and reverse reactions of equation (1) are typical acid–base reactions and in Table IV are recorded rate constants covering a range of twenty-four powers of ten. These include rates which are far too slow to measure (half-lives of thousands of years), rates which are as fast as the reactants can diffuse toward each other and collide, and all possible values in between. Thus there seems to be no evidence for Lewis and Seaborg's sharp distinction into primary and secondary acids and bases. Rather we have a gradual transition from slowly reacting, or pseudo, acids and bases to rapidly reacting, or normal, acids and bases.

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(36) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

(37) See G. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, Chapter VI.

(38) G. N. Lewis and G. T. Seaborg, THIS JOURNAL, **61**, 1886 (1939); G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

Sexadentate Chelate Compounds. VI

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The bis-salicylidene derivatives of 1,9-diamino-3,6-dithianonane (EET base) and 1,10-diamino-3,7-dithiadecane (ETT base) have been prepared and caused to react with cobalt salts to give crystalline complex cobalt(III) salts whose structures have been correlated with those of the bases from which they are derived.

Extension of the arguments put forward in Part III[3] of this series of papers to the structure of the complex ions derived from cobalt(III) and the sexadentate chelate compounds prepared by condensing salicylaldehyde with 1,9-diamino-3,6-dithianonane (EET base) and 1,10-diamino-3,7-dithiadecane (ETT base) would strongly suggest that the former should be capable of existence only in enantiomorphous forms structurally similar to those obtained from the bis-salicylidene derivative of EEE base,[4] whilst there could be the possibility of the latter existing in two structurally isomeric pairs of enantiomorphs. Experiment has now shown that the facts agree with this prediction.

At one end of the molecule of EET base there is an ethylene chain between the nitrogen atom and the sulfur atom. At the other end the second nitrogen atom is separated from the other sulfur atom by a trimethylene chain. For convenience the former may be designated the E end and the latter the T end of the molecule. When a molecule of the bis-salicylidene derivative of EET base loses two protons and wraps itself round a triply positively charged cobalt atom it should be possible, arguing on analogy with the complexes derived from TET base, for the oxygen–nitrogen–sulfur atom sequence at the T end of the molecule to take up one or the other of two configurations. In one the oxygen, nitrogen and sulfur atoms would lie

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[3] F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, THIS JOURNAL, **74**, 4188 (1952).

[4] *Cf.* Part I, F. P. Dwyer and F. Lions, *ibid.*, **72**, 1545 (1950).