Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.13; H, 7.17.

TABLE I

MOLECULAR EXTINCTION COEFFICIENTS OF *cis-cis*-DIPHENYLBUTADIENE AT THE MAXIMA (*italicized*) AND MINIMA

Solvent	*cis-cis* form		Mixture of stereoisomers upon iodine catalysis	
	mμ	$E^{\text{mol.}}_{\text{1 cm.}} \times 10^{-4}$	mμ	$E^{\text{mol.}}_{\text{1 cm.}} \times 10^{-4}$
Hexane	*299–300*	2.96	*344–345*	3.40
	251	0.51	340	3.35
			328	5.36
			318–319	4.50
			315–316	4.56
			255	0.20
			230–231	1.36
Benzene	*306*	2.67	*352–353*	3.17
			347	2.95
			334–335	4.85
			325–326	4.00
			321–322	4.05

Small-Scale Separation of the Three Stereoisomeric Diphenylbutadienes.—A solution which contained 1 mg. of each isomer in 10 ml. of petroleum ether was developed with the same solvent on alumina (20 × 2 cm.); the developer was forced through the column by nitrogen pressure in order to avoid partial evaporation of the filtrate. The fluorescent *trans-trans* compound remained near the top. Small samples of each fraction collected from the filtrate were submitted to the iodine-catalysis and fluorescence test as described. The first 120 ml. of the flow were found to be free of substance; subsequent 5-ml. fractions were tested with the following result ("*cis-cis*" or "*cis-trans*" refer to the configuration before iodine catalysis):

No. 1–7, strong fl.: *cis-cis*
8–9, weak fl.: *cis-cis*
10–12, almost no fl.: traces
13–21, very strong fl.: *cis-trans*
22–26, strong fl.: *cis-trans*
27–30, weak fl.: *cis-trans*
31, no fl.

The fractions were also tested spectroscopically; the extinction curves of fractions 3 and 16 are given in Fig. 10.

Summary

A comparative study of the *trans-trans*-, *cis-trans*-, and *cis-cis*- forms of 1,4-diphenylbutadiene is presented. The relative stability of the respective configurations depends on the nature of the photochemical or thermal treatment. Data characterizing the spectroscopic and chromatographic behavior are given, and the stereoisomeric diphenylbutadienes are compared with some spatial types of the carotenoids.

PASADENA, CALIFORNIA RECEIVED DECEMBER 20, 1947

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WESTERN AUSTRALIA]

Isopiestic Measurements on the Primary Sodium and Potassium Salts of Malonic, Succinic and Adipic Acids at 25°

BY JEAN M. STOKES[1]

The order of the activity coefficient curves for the alkali formates, acetates, and hydroxides is Li < Na < K, a reversal of the usual order K < Na < Li which holds for the halides and many other salts. To account for this, Robinson and Harned[1a] have advanced an hypothesis of "localized hydrolysis," according to which anion and cation are "associated" through interaction with a polarized water molecule, an effect which may be expected to depend on the proton-accepting power of the anion. In order to study this effect for salts of acids of different strengths, the primary sodium and potassium phosphates have been investigated.[2] It was found, however, that these two salts had very low activity coefficients and ionic association probably occurred to a marked extent. Indeed, the primary phosphate ion seems to belong to what Scatchard[3] has termed the second class of anions, in which he included the nitrate, chlorate and perchlorate ions and to which recent measurements[4] indicate the bromate ion should be added.

Measurements are now reported on the salts of three acids of dissociation constant ranging from 10^{-3} to 10^{-6}.

Experimental

Solutions of the sodium and potassium salts of malonic, succinic and adipic acid were prepared by (a) half neutralization of the purified acid with hydroxide in aqueous solution and (b) precipitation of solid salt from alcoholic solutions of acid and base, digestion with alcohol and subsequent solution in water. The two methods gave similar results but the experimental points did not lie on a smooth isopiestic curve as well as other salts that have been investigated. This may be due to sensitivity to the exact composition of the alkali hydrogen salt or to the *p*H of the solution; high accuracy is not claimed for these results, but they are probably accurate to 1% and the order and position of the activity coefficient curves is therefore significant. The molalities of isopiestic solutions are given in Table I and the osmotic and activity coefficients calculated with the aid of the data for the reference salt, sodium chloride,[5] are given in Table II.

Discussion

The activity coefficient curve of sodium hydrogen adipate is close to that of potassium iodide while the potassium salt resembles potassium bromide; sodium and potassium hydrogen succinate are comparable with rubidium chloride and cesium bromide, respectively; sodium hydrogen malo-

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[1a] R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 419 (1941).

[2] J. M. Stokes, *Trans. Faraday Soc.*, **41**, 685 (1945).

[3] G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 807 (1934).

[4] J. H. Jones, *ibid.*, **65**, 1353 (1943); **66**, 1672 (1944).

[5] R. H. Stokes and B. J. Levien, *ibid.*, **68**, 333 (1946).

nate also resembles cesium bromide but the potassium salt exhibits very low activity coefficients comparable with those of sodium bromate.

TABLE I

ISOPIESTIC SOLUTIONS OF SODIUM CHLORIDE AND SODIUM AND POTASSIUM HYDROGEN MALONATE, SUCCINATE AND ADIPATE

M_{NaCl} = molality of sodium chloride. M_X = molality of other salt

M_X	M_{NaCl}	M_X	M_{NaCl}	M_X	M_{NaCl}
Sodium hydrogen malonate					
0.3995	0.3850	0.4305	0.4141	0.9282	0.8676
1.407	1.277	1.799	1.605	2.131	1.863
2.247	1.960	2.850	2.422	3.080	2.573
3.451	2.855	3.849	3.125	4.765	3.727
Potassium hydrogen malonate					
0.2577	0.2498	0.2623	0.2534	0.3910	0.3734
0.6906	0.6322	1.643	1.388	1.697	1.432
1.996	1.655	2.747	2.183	3.741	2.812
4.156	3.044	4.206	3.080	4.996	3.506
5.035	3.530				
Sodium hydrogen succinate					
0.2345	0.2296	0.2831	0.2771	1.193	1.116
1.248	1.167	1.650	1.516	1.931	1.764
2.300	2.081	2.449	2.206	2.897	2.573
3.717	3.232	4.010	3.467	4.935	4.176
Potassium hydrogen succinate					
0.2592	0.2512	0.3183	0.3062	0.5440	0.5168
0.6900	0.6480	0.8451	0.7848	1.123	1.021
1.823	1.601	2.334	2.010	2.530	2.163
2.775	2.353	3.663	3.035	3.848	3.165
4.398	3.553				
Sodium hydrogen adipate					
0.3132	0.3116	0.3441	0.3424	0.4253	0.4224
0.6600	0.6510	0.6863	0.6767		
Potassium hydrogen adipate					
0.2730	0.2690	0.3677	0.3622	0.4576	0.4490
.5700	.5546	.7173	.6950	.7875	.7645
.8451	.8173	.9310	.8970	.9380	.9050
				.9730	.9355

If the reversal of order of the activity coefficient curves of the acetates, etc., is associated in any way with the strength of the acid from which the salt is derived, since the dissociation constants of malonic, succinic and adipic acid are 1.6×10^{-3}, 6.7×10^{-5} and 3.6×10^{-5}, respectively, a reversal of order might be expected with the succinates and adipates but not with the malonates. Figure 1, in which the activity coefficients are plotted, along with those for the acetates, shows that there is no reversal of order with these salts, although the difference between the curves for sodium and potassium hydrogen succinate and adipate is small compared with that found for the halides. This plot, however, does show that there is a difference

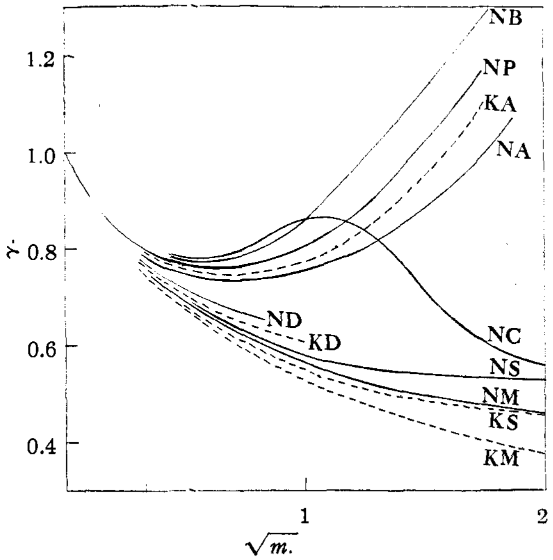

Fig. 1.—Comparison of activity coefficients of the sodium and potassium salts of some simple organic acids: NB, sodium butyrate; NP, sodium propionate; KA, potassium acetate; NA, sodium acetate; ND, sodium adipate; KD, potassium adipate; NC, sodium caproate; NS, sodium succinate; NM, sodium malonate; KS, potassium succinate; KM, potassium malonate.

TABLE II

OSMOTIC AND ACTIVITY COEFFICIENTS AT 25°

	Malonates				Succinates				Adipates			
	K salt		Na salt		K salt		Na salt		K salt		Na salt	
m	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
0.1	0.920	0.759	0.923	0.764	0.922	0.762	0.924	0.765	0.928	0.772	0.931	0.776
.2	.903	.702	.907	.709	.904	.705	.910	.712	.917	.724	.921	.730
.3	.891	.665	.896	.674	.892	.668	.898	.677	.909	.693	.917	.703
.5	.866	.610	.880	.626	.875	.619	.888	.635	.900	.654	.912	.670
.7	.847	.570	.872	.595	.867	.588	.882	.607	.898	.631	.911	.650
1.0	.829	.528	.863	.563	.856	.553	.878	.579	.899	.609		
1.5	.807	.480	.857	.528	.846	.516	.879	.552				
2.0	.799	.450	.856	.507	.845	.493	.887	.538				
2.5	.792	.427	.855	.490	.848	.478	.895	.529				
3.0	.785	.408	.855	.477	.854	.468	.907	.526				
3.5	.778	.392	.855	.467	.865	.463	.917	.524				
4.0	.771	.377	.856	.458	.870	.457	.929	.525				
4.5	.764	.365	.857	.451	.876	.453	.942	.528				
5.0	.757	.353	.858	.445			.958	.534				

between salts of the type $COOH(CH_2)_nCOONa$ and $CH_3(CH_2)_nCOONa$, a difference which is marked in spite of the anomalous behavior of sodium caproate[6] at high concentration (probably due to micelle formation). Along with this difference between the two types of salts are to be noted the very low values of the activity coefficients of the salts now under investigation, suggesting that the hydrogen malonate, succinate and adipate ions belong to the same category as the nitrate, chlorate and primary phosphate ions. Thus, although "localized hydrolysis" may be a factor resulting in decreasing dispersion of the curves of the sodium and potassium salts as we proceed from the malonate to the adipate, there must be another factor of larger magnitude which lowers the curves of both the sodium and the potassium salts. It is difficult to explain this effect for the nitrate ion and it is equally difficult to understand why it should occur with ions of the hydrogen malonate type; furthermore, it is difficult to find a common factor between nitrates and malonates apart from their low activity coefficients.

I wish to thank Professor N. S. Bayliss for his kind permission to use the facilities of his department.

Summary

Isopiestic measurements have been made on solutions of the primary sodium and potassium salts of malonic, succinic and adipic acid and the osmotic and activity coefficients calculated.

Although these salts are derived from weak acids, their activity coefficient curves are in the order Na > K; in this respect they differ from the sodium salts of monobasic fatty acids. Moreover, their activity coefficients are very low and have an unexpected resemblance in this respect to sodium and potassium nitrate and the primary phosphates.

NEDLANDS, WESTERN AUSTRALIA
RECEIVED FEBRUARY 4, 1948

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[6] E. R. B. Smith and R. A. Robinson, *Trans. Faraday Soc.*, **38**, 70 (1942).

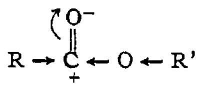
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Effect of Structure on Reactivity.[1] I. Ammonolysis of Esters with Special Reference to the Electron Release Effects of Alkyl and Aryl Groups

BY MAXWELL GORDON,[2] JOHN G. MILLER AND ALLAN R. DAY

In the interest of augmenting present knowledge of the effect of structure on reactivity, it was decided to measure the rates of ammonolysis of several homologous series of esters. Although several reports have appeared in the literature on the effect of structural variations on the rate of ammonolysis of esters, they have embraced only limited numbers of esters, the possibility of ester interchange in working in alcoholic solution was often overlooked, no calculations of rate constants or activation energies were made in many cases, and the conclusions derived from these studies were, in some instances, conflicting. Most of the references in the literature on this subject have been discussed by Gorvin.[3] Additionally it has been shown by Komatsu and Nakayama[4] that ethyl phenylacetate reacts with ammonia fifteen times as rapidly as does ethyl benzoate.

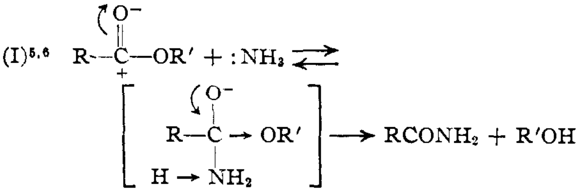
The present study of the ammonolysis of esters was undertaken in an effort to show the effect of various R and R′ groups in the ester RCOOR′, with special emphasis on tracing the electron release effects in various homologous series. Most of the mechanisms which have been postulated for ammonolysis or hydrolysis of esters[5] indicate that the reactivity of the ester depends on the polarization of the carbonyl group in the ester which then provides the center for nucleophilic attack at the carbon of the carboxyl group. From this representation it may be seen that the greater



$$R \rightarrow \overset{\overset{O^-}{\|}}{\underset{+}{C}} \leftarrow O \leftarrow R'$$

the electron release of the R or R′ group, the slower should be the rate of ammonolysis of the ester since the positive charge on the carbonyl carbon would be reduced in magnitude.

One may consider two possible mechanisms for the ammonolysis of esters



$$(I)^{5,6}\quad R-\overset{\overset{O^-}{\|}}{\underset{+}{C}}-OR' + :NH_3 \rightleftharpoons \left[\begin{array}{c} O^- \\ | \\ R-C \rightarrow OR' \\ | \\ H \rightarrow NH_2 \end{array}\right] \longrightarrow RCONH_2 + R'OH$$

Betts and Hammett[7] suggested that both the am-

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[1] From a thesis submitted by M. Gordon to the Department of Chemistry and Chemical Engineering of the University of Pennsylvania, Dec. 1947, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] National Institute of Health Predoctoral Research Fellow, 1946–1948.

[3] Gorvin, *J. Chem. Soc.*, 732 (1945).

[4] Komatsu and Nakayama, *J. Chem. Soc.* (*Japan*), **54**, 558–569 (1933).

[5] H. Meyer, *Monatsh.*, **27**, 31 (1906); Holmberg, *Ber.*, **45**, 2997 (1912); Ingold and Ingold, *J. Chem. Soc.*, 758 (1932); Polanyi and Szabo, *Trans. Farad. Soc.*, **30**, 508 (1934); Day and Ingold, *ibid.*, **37**, 689 (1941); Watson, *ibid.*, **37**, 712 (1941).

[6] Chattaway, *J. Chem. Soc.*, 355 (1936).

[7] Betts and Hammett, THIS JOURNAL, **59**, 1568 (1937).