<div align="center">TABLE VII</div>

<div align="center">IONIZATION HEATS OF GLYCINE AND dl-ALANINE AT 25°</div>

		Glycine			dl-Alanine		
		E. m. f.		Calorimetric	E. m. f.		Calorimetric
ΔH_A^0	joules per mole	$4915^{b,c}$	4602^d	3891^e	$3368^{f,c}$	3347^g	2585^h
	calories[a] per mole	$1175^{b,c}$	1100^d	930^e	$805^{f,c}$	800^g	615^h
ΔH_B^0	joules per mole	$11570^{b,c}$	11710^d	11591^e	$10713^{f,c}$	7605^g	10540^h
	calories[a] per mole	$2765^{b,c}$	2800^d	2771^e	$2561^{f,c}$	1818^g	2520^h

[a] One calorie (defined) = 4.1833 international joules. [b] Owen. THIS JOURNAL, **56**, 24 (1934). [c] Harned and Owen, *Chem. Rev.*, **25**, 31 (1939). [d] Recalculation of Owen's data by Everett and Wynne-Jones. *Trans. Faraday Soc.*, **35**, 1380 (1939). [e] Sturtevant. ref. 1. [f] Smith, Taylor and Smith. *J. Biol. Chem.*, **122**, 109 (1937). [g] Recalculation of data of Smith. Taylor and Smith by Everett and Wynne-Jones. ref. *d*. [h] Present research.

higher than that for alanine, while the calorimetric value for glycine is about 51% higher. Thus this large difference between glycine and alanine can be considered as firmly established.

If we consider ZH^+ as a dibasic acid, then its ionization heats are related to ΔH_A^0 and ΔH_B^0 as follows: $\Delta H_{A_1}^0 = \Delta H_A^0$; $\Delta H_{A_2}^0 = \Delta H_W^0 - \Delta H_B^0$. Taking the value $\Delta H_W^0 = 55,881$ joules per mole given by Pitzer,[16] we obtain $\Delta H_{A_2}^0 = 45,341$ joules per mole, or 10,838 defined calories per mole.

(16) Pitzer. THIS JOURNAL. **59**. 2365 (1937).

Summary

Calorimetric measurements of the heats of neutralization of *dl*-alanine by hydrochloric acid and sodium hydroxide at 25° are reported. A double extrapolation of the results is employed to give values of the acidic and basic ionization heats. The heat of the acid ionization of alanine is about two-thirds that of glycine, while the heat of the basic ionization of alanine is about nine-tenths that of glycine.

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The Dipole Moments and Structures of Diketene and of Certain Acid Anhydrides and Related Oxygen and Sulfur Compounds

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The dipole moments of diketene, benzoic anhydride, benzoyl peroxide, benzoyl persulfide, and diphenyl sulfone have been measured in benzene solution in order to study their molecular structures. These structures have in common the fact that carbonyl or sulfone groups may rotate about some axis in them giving rise to the possibility of change in dipole moment, which may be influenced by steric hindrances, resonance or both.

Purification of Materials

Diketene.—A sample, kindly presented to us by Dr. A. B. Boese of the Carbide and Carbon Chemicals Corporation, was brought by hand from Pittsburgh and kept at low temperature until the measurements were made.

Benzoic Anhydride.—Material from the Eastman Kodak Company was used without purification; m. p. 43°.

Benzoyl Peroxide.—Material from the Eastman Kodak Company was recrystallized from alcohol; m. p. 104–105°.

Benzoyl Persulfide.—Material from the Eastman Kodak Company was recrystallized from ether: m. p. 127–128°.

Diphenyl Disulfone.—A sample was kindly given us by Dr. H. E. Westlake.

Benzene.—The purification was carried out in the usual manner.[1] The dielectric constant and density of the benzene were measured every day on which the solutions in it were run, the values being given in Table I.

Experimental Results

The dielectric constants, ϵ, at 520 kilocycles and the densities, d, of benzene solutions containing mole fractions c_2 of the polar compound were measured as in previous work.[2] The data are listed in Table I, together with the polarizations calculated from them. Table II lists in the second column the values of MR_D, the molar refraction for the D sodium line, the value for diketene being

(1) Smyth and Walls. THIS JOURNAL. **54**. 1854 (1932).
(2) Lewis and Smyth. *J. Chem. Phys.*. **7**. 1085 (1939); THIS JOURNAL. **61**. 3063 (1939).

the one measured by Chick and Wilsmore,[3] the value for benzoic anhydride being calculated from the atomic and molar refractions given in Landolt–Börnstein, and the values for the other three substances being calculated from density and refractive index measurements made upon their benzene solutions. The third column gives the polarizations, P_∞, obtained by extrapolation to $c_2 = 0$ of the values of P_2 in Table I and the fourth column gives the dipole moments calculated in the usual manner. The probable error of the few measurements on benzoyl persulfide is large, giving an uncertainty of 10% in the moment values. The errors in the other four moment values should be less than 1%. The value for diketene agrees satisfactorily with those, 3.15 in benzene, 3.30 in carbon tetrachloride, in the literature.[4] The mo-

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF BENZENE SOLUTIONS AND POLARIZATIONS

| c_2	ϵ	d	P_2
Diketene (25°)			
0.00000	2.2807	0.87251	...
.01331	2.4826	.87493	235
.02026	2.5862	.87609	229
.03663	2.8415	.87915	221
.05796	3.1621	.88303	207
.08323	3.5451	.88731	194
Benzoic Anhydride (25°)			
0.00000	2.2769	0.87403	...
.01010	2.5215	.88097	395
.02210	2.8177	.88816	383
.03807	3.2128	.89966	364
.07136	4.0740	.92036	336
Benzoyl Peroxide (45°)			
0.00000	2.2347	0.85191	...
.02095	2.3036	.86778	109
.03453	2.3452	.87808	108
.06380	2.4423	.90027	108
Benzoyl Persulfide (25°)			
0.00000	2.2813	0.87395	...
.01098	2.3099	.88500	101
.01811	2.3315	.89225	103
Benzoyl Persulfide (45°)			
0.00000	2.2347	0.85191	...
.01934	2.3142	.86941	(128)
.04040	2.3492	.88847	109
Diphenyl Disulfone (25°)			
0.00000	2.2769	0.87398	...
.00164	2.3142	.87594	392
.00000	2.2763	.87388	...
.00253	2.3329·	.87702	383

(3) Chick and Wilsmore. J. Chem. Soc., **93**. 946 (1908).

(4) Angus, Leckie, LeFèvre, LeFèvre and Wassermann, ibid., 1751 (1935).

ments of a number of related compounds taken from the literature are added for the sake of comparison.

TABLE II

MOLAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Substance	MR_D	P_∞	$\mu \times 10^{18}$
$CH_3COCHCO$	20.1[3]	244 (25°)	3.31
$(C_6H_5CO)_2O$	62	414 (25°)	4.15
$(C_6H_5CO_2)_2$	63	110 (45°)	1.58
$(C_6H_5COS)_2$	80	103 (25°)	1.1
		120 (45°)	1.4
$(C_6H_5SO_2)_2$	75	390 (25°)	3.93
$(CH_3CO)_2$			1.25 (46°)–
			1.48 (231°)[5]
$(CH_3CO)_2CH_2$			2.9[6,7]
$(C_7H_{15}CO)_2C_7H_{14}$			3.6[8]
$(C_6H_5CO)_2$			3.6[9,10,11]
$(CH_3CO)_2O$			2.8[6,12]
$(CH_2CO)_2O$			4.2[13]
$CH_3C:CH:C_2O_3$			4.3[13]
$C_6H_4C_2O_3$			5.3[13]
$(C_6H_4CO)_2O$			5.3[14]

Discussion of Results

Angus, Leckie, LeFèvre, LeFèvre and Wassermann[4] investigated the dipole moment, the heat of formation, and other physical properties of diketene and decided that the most probable of the three cyclic structures shown was II, for which
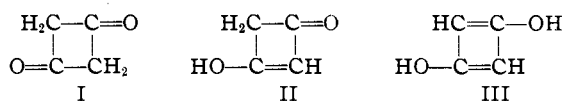

they calculated a moment close to the observed value. Their conclusion was that II represented the structure, with possible small amounts of I and III present. From chemical behavior and parachor determination, Hurd and Williams[15] concluded the structure to be that of acetylketene IV or β-crotonolactone V.
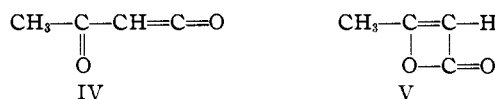
Hurd and Roe[16] indicated an equilibrium mixture of the two forms IV and V as probable, while

(5) Zahn, Phys. Rev., **40**. 291 (1932).

(6) Zahn, ibid., **34**. 570 (1933).

(7) Wolf, Physik. Z., **31**, 227 (1930).

(8) Ebert and Højendahl, Z. physik. Chem., **B15**. 74 (1931).

(9) Hassel and Naeshagen, ibid., **B6**, 152 (1929).

(10) Sängewald and Weissberger, Physik. Z., **30**, 268 (1929).

(11) Higasi, Bull. Chem. Soc. Japan, **13**, 158 (1938).

(12) Piekara and Piekara, Compt. rend., **198**, 1018 (1934).

(13) Rau and Anatanarayanan, Proc. Indian Acad. Sci., **5A**, 185 (1937).

(14) LeFèvre and Vine, J. Chem. Soc., 967 (1938).

(15) Hurd and Williams, THIS JOURNAL, **58**, 962 (1936).

(16) Hurd and Roe, ibid., **61**, 3355 (1939).

Boese adopted vinylaceto-β-lactone, VI, as a preferred structure.

$$CH_2\!\!=\!\!C\!\!-\!\!CH_2$$
$$| \quad |$$
$$O\!\!-\!\!CO$$
$$VI$$
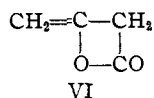
From measurements of absorption spectra, Calvin, Magel and Hurd[17] have just concluded that the β-crotonolactone formula, V, is most probable, together with the condition of extremely easy transformation into the isomeric acetylketene form, IV. Unfortunately, the dipole moment does not provide a unique solution of the problem of these structures. With free rotation around the single bonds and bond moments 2.5 and 0.4 for C=O and H—C, respectively, the moment of structure IV is calculated[18] as 3.4, just above the observed value 3.3. Lowering of the two bond moments to the slightly more probable values 2.4 and 0.3 lowers the calculated value just below the observed. In other words, structure IV would have a moment agreeing within the accuracy of the calculation with that observed for diketene. For structures V and VI, the moment may be estimated roughly by treating the ring as a square with a moment equal to that of trimethylene oxide, 2.0,[19] acting along one diagonal and a moment equal to that of acetone, 2.7,[20] acting along the other diagonal. The resultant, 3.4, is in excellent agreement with the observed moment of diketene, 3.3. Of course, the unknown deviations from the square structure and inductive effects would change both the angles and the moments somewhat, but should not change the resultant greatly. It is thus evident that, although the dipole moment of the molecule eliminates structures I and III, it does not distinguish between the other four structures. As far, then, as the dipole moment evidence goes, the β-crotonolactone structure is as probable as any.

The use of atomic models indicates that steric repulsion should not be large in the molecule of diacetyl or dimethyl diketone. However, LuValle and Schomaker[21] have concluded from electron diffraction measurements that the molecule is essentially co-planar and *trans* with the carbon–carbon bond connecting the adjacent carbonyl groups shortened by an amount corresponding to

15 or 20% double bond character and with the amplitude of any libration around this bond small. Their energy calculations indicate that, if the molecules were distributed between a *cis* and a *trans* configuration, only about 5% would be in the *cis* form. The small moment value, much lower than that calculated[18] on the assumption of free rotation, is consistent with these results, while its rise from 1.25 at 46° to 1.48 at 231° indicates the increase to be expected in the amplitude of the libration or in the proportion of the *cis* form as the temperature rises. Separation of the two carbonyl groups, which are responsible for the moment, by a single carbon atom raises the moment to 2.9, while separation by seven carbon atoms, which must eliminate repulsion between the two carbonyl groups, raises the moment to 3.6 in fair agreement with the calculated value 3.8. It is surprising, at first glance, to find the moment tripled by the replacement of the methyls of diacetyl by phenyls to give benzil, which has a moment little smaller than what one would calculate for it in the absence of any very pronounced resonance effect. This suggests a decrease in the amount of double bond character in the carbonyl-carbonyl bond, presumably because of contributions from structures with a carbonyl carbon linked by a double bond to a positively charged ring, the oxygen acquiring the corresponding negative charge. The replacement of the contributions from structures containing a double bond between the carbonyl carbons by structures containing a double bond between one or the other of these carbons and an attached benzene ring would make possible a rotation of the two halves of the molecule relative to one another. Although this rotation should be hindered by steric repulsion, the resultant moment should be much larger than that found for diacetyl and might easily approach the calculated value.

The acid anhydrides may be conveniently examined by assigning bond moments as before, and calculating a resultant for the acetate group. This resultant moment 2.5 makes an angle of 99° with the C—O bond, which is the axis around which rotation of the group moment may occur. The rough approximation of setting this angle equal to 90° instead of 99° facilitates the moment calculations without invalidating the rough conclusions to be drawn. The moment calculated on this basis for acetic anhydride is simply $2.5 \sqrt{2} = 3.5$. The observed value 2.8 suggests that re-

(17) Calvin, Magel and Hurd, THIS JOURNAL, **63**, 2174 (1941).

(18) Eyring, *Phys. Rev.*, **39**, 746 (1932); Smyth and Walls, THIS JOURNAL, **54**, 2261 (1932).

(19) Allen and Hibbert, THIS JOURNAL, **56**, 1398 (1934).

(20) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

(21) LuValle and Schomaker, THIS JOURNAL, **61**, 3520 (1939).

pulsion may reduce the probability of occurrence of certain configurations of larger than average moment. In succinic and citraconic anhydrides, the two formerly movable dipoles are fixed on one side of the molecule. Assumption that they are in the same plane with the same valence angles as before leads to a calculated moment value, 4.1, in good agreement with the observed values, 4.2 and 4.3.

The moment of benzoic anhydride, 4.15, shows a great increase over that of acetic anhydride, 2.8, just as that of benzil showed a great increase over that of acetyl. Qualitatively, this increase in moment may be attributed to contributions in which, as before, the carbonyl oxygen acquires a negative charge from the ring, which becomes a quinoid structure with a positively charged carbon. It may, however, be objected that contributions from such structures have only a small effect in benzoic acid and the phenyl ketones. The increased moment resulting from the presence of the aromatic ring is again evident in the moments of phthalic and diphenic anhydrides which are a unit higher than those of succinic and citraconic anhydrides.

The moment of benzoic anhydride is about what would be expected if there were small resonance contributions from the just-mentioned polar forms and complete freedom of rotation around the C—O bonds. The molecular model, however, gives no indication of greater rotational freedom than in acetic anhydride. The insertion of another oxygen to form benzoyl peroxide might be expected to give greater rotational freedom, although, of the many configurations conceivable for it, some are ruled out by steric hindrance. Use of the same approximations as in the previous calculations gives a moment value for the peroxide equal to that for the anhydride, as it should contain the same dipoles and bond angles as the latter. It is surprising, then, to find a moment for the peroxide less than half that for the anhydride. The structure of the persulfide should be similar to that of the peroxide and the moments

of the two molecules should differ only because of the small difference 0.1 between the C—O and the C—S bond moments.[22] The rough values found for the persulfide are only slightly smaller than that for the peroxide, and their apparent increase with increasing temperature suggests that they are low because of internal repulsion, which is partially overcome as the temperature rises.

The moment of the sulfone group as calculated by Martin and Partington[23] is 3.6, the difference between the moments of diphenyl sulfone and diphenyl sulfide. If the diphenyldisulfone molecule consists of two tetrahedra with a sulfur atom at the center of one linked to a sulfur at the center of the other by a bond which passes through a shared apex of each with free rotation about this bond, the moment value calculated for the molecule is 4.6. The slightly lower observed value 3.9 may indicate some restriction of rotation, difference in resonance effects, or alteration of the bond angles, but the discrepancy is not large.

Summary

The dipole moments of diketene, benzoic anhydride, benzoyl peroxide, benzoyl persulfide, and diphenyl disulfone have been measured in benzene solution. The moment of diketene agrees closely with the values calculated for its most probable structures and does not serve to distinguish between them. The cyclic acid anhydrides have larger moments than similar alicyclic anhydrides because their major dipoles are forced by the rings to point more nearly in the same direction. The aromatic anhydrides have their moments increased by resonance contributions from highly polar structures. The peroxide and persulfide have much lower moments than the anhydrides. The disulfone has a large moment consistent with a structure consisting of two tetrahedra sharing an apex.

(22) Smyth, THIS JOURNAL, 60, 183 (1938).

(23) Martin and Partington, J. Chem. Soc., 1182 (1936).