

Predictions of the Enthalpies of Protonation of Amines. Log K, ΔH, and ΔS Values for the Protonation of Ethylenediamine and Tri-, Tetra-, Penta-, and Hexa-methylenediamine †

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Values of the thermodynamic functions ΔG , ΔH , and ΔS for the protonation of the polymethylenediamines $H_2N(CH_2)_nNH_2$ ($n = 2-6$), i.e. ethylenediamine and tri-, tetra-, penta-, and hexa-methylenediamines have been determined, by means of potentiometric and calorimetric measurements at 25° in 0.5M-potassium nitrate solution. The variations in the values of the thermodynamic functions along the series have been interpreted in terms of the following: (i) the effect of the substituents NH_2 or NH_3^+ , (ii) the length of the aliphatic chain, (iii) solute-solvent hydrogen-bond formation, and (iv) the rigidity of the aliphatic chain. A formula for predicting the heats of protonation of aliphatic mono- and di-amines is proposed.

RECENTLY, interest in protonation and in the corresponding thermodynamic functions has increased steadily. A considerable amount of work has been carried out on carboxylic acids,¹ and, recently, on amines. For example, Clark and Perrin² have suggested a formula for the calculation of the basicity constant of the nitrogen atom in any amine, to a good approximation, based mainly on the assumption that the influence of a substituent on the basicity of the nitrogen atom is halved in passing from one position to the next. A recent review by Christensen *et al.*³ reported a large number of enthalpies and entropies of protonation for organic bases. These results indicated that protonation does not show the linear relationship between ΔG and ΔS predicted by Bjerrum's electrostatic theory.⁴ They put forward a formula for predicting the enthalpies and entropies of protonation for primary and secondary monoamines. We have previously reported⁵ the potentiometric determination of the basicity constants of ethylenediamine (en) and trimethylenediamine (tn) in 0.5M-potassium nitrate at 25°.

The relative enthalpies of protonation were determined calorimetrically under the same conditions. We have now extended this work to tetramethylenediamine (putrescine) (put), pentamethylenediamine (cadaverine) (cad), and hexamethylenediamine (hen). The heats of protonation of trimethylenediamine were checked with a titration calorimeter.

The data in the literature^{3,6} on these systems refer to different ionic media, temperatures, and methods of determination. Starting with an assumption similar to that of Clark and Perrin² for the basicity constants, we have obtained a formula which allows the prediction, to a good approximation, of the enthalpies of protonation of aliphatic primary mono- and di-amines.

EXPERIMENTAL

Materials.—All the compounds used were of commercial origin (Fluka puriss.). Trimethylenediamine was purified

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¹ J. J. Christensen, J. L. Oscarson, and R. M. Izatt, *J. Amer. Chem. Soc.*, 1968, **90**, 5949; and references therein.

² J. Clark and D. D. Perrin, *Quart. Rev.*, 1964, **18**, 295.

³ J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc. (A)*, 1969, 1212.

as previously described.⁵ Putrescine and cadaverine were fractionally distilled with a Todd column and only the middle fraction was used. In each case gas chromatography on a column packed with Celite and silicone oil DC 200 showed only one peak, corresponding to the amine in question. Potentiometric titration of putrescine with 1M-nitric acid showed that it was 99.9% pure and this material was used to prepare solutions. Cadaverine was further distilled under reduced pressure until titration showed that it was 99.8% pure. Hexamethylenediamine was not purified since titration of the commercial product showed that it was 99.7% pure and this was considered to be satisfactory.

Solutions of the diamines were prepared in water which had been twice distilled and decarbonated. Their concentrations were determined by potentiometric titration against standard nitric acid. Cadaverine hydrochloride was prepared by adding hydrochloric acid to an aqueous alcoholic solution of the amine. The product was recrystallized from aqueous alcohol and then dried to constant weight at 60° *in vacuo* (Found: Cl, 40.4. $C_5H_{16}Cl_2N_2$ requires C, 40.5%).

E.m.f. Measurements.—The apparatus for the potentiometric measurements has been described elsewhere.⁵ For each determination, the cell contained *ca.* 100 ml. of a solution of 0.5M-potassium nitrate in which known amounts of the amine and acid were dissolved. For cadaverine, however, the hydrochloride was used directly. The solution was titrated with 0.5M-potassium hydroxide solution added from a Metrohm Dosimat E 415 automatic piston burette.

Experimental details and a typical curve are shown in Table 1. The effects due to the liquid junction potential and to the potential drift of the electrode during the measurements were shown to be negligible for the range of pH under consideration; the maximum values of these effects were of the same order as the experimental error of the potentiometer (0.2 mv).

The ionic product of water was determined in 0.5M-potassium nitrate; the value found (pK_w 13.71) is in good agreement with that previously found.⁶ The basicity constants were calculated from data from at least two different titration curves for each amine. The method used

⁴ E. J. King in 'Acid-Base Equilibria,' vol. 4, ed. R. A. Robinson, Macmillan, New York, 1965, Topic 15 of the International Encyclopaedia of Physical Chemistry and Chemical Physics, p. 210.

⁵ A. Vacca and D. Arenare, *J. Phys. Chem.*, 1967, **71**, 1495.

⁶ L. G. Sillén and A. E. Martell, 'Stability Constants,' *Chem. Soc. Spec. Publ.* 1964, 17, The Chemical Society, London, 1964.

has been described elsewhere.⁷ Experimental data are available on request from the authors.

Calorimetric Measurements.—An LKB 8700-2 titration calorimeter was used, calibrated with aminotris(hydroxymethyl)methane (tham). The result from three different runs was 11.234 ± 0.007 kcal. mole⁻¹; other authors,⁸ using an indirect method, found 11.364 kcal. mole⁻¹. We

of the diamine. A Metrohm Dosimat E 415 automatic burette was in conjunction with a Metrohm Dosifix E 442 programmer. All measurements were carried out with the reaction system thermostatted at $25.000^\circ \pm 0.001^\circ$. The heats of protonation were calculated with an IBM 1620 computer and an appropriate FORTRAN programme.⁷ The detailed results are shown in Table 2.

TABLE I
Experimental details of the potentiometric measurements

Curve	Amine	HNO ₃	Initial conc. (M $\times 10^3$)	Range	
				—log [H ⁺]	g
1	put	7.093	19.04	7.87—11.02	1.98—0.40
2	put	7.093	19.20	8.43—11.05	1.94—0.38
3	cad	9.813	19.63	8.78—10.97	1.95—0.55
4	cad	9.540	19.08	8.80—10.96	1.94—0.56
5	cad	10.020	20.04	8.81—10.96	1.94—0.56
6	hen	6.541	22.02	2.66—11.18	2.00—0.49
7	hen	7.089	22.09	2.58—11.16	2.00—0.50

CURVE I Amount of nitric acid = 2.074 mmoles, and of put = 0.772 mmole; initial volume = 108.9 ml.; $E_0 = 272.8$ mv; [KOH] = 0.498 M; and $U = 0.001644$ (ml.).²

KOH (ml.)	E (mv)	Residual (ml.)	g	—log [H ⁺]
1.10	-192.6	0.011	1.983	7.867
1.20	-234.2	0.011	1.920	8.570
1.30	-251.0	0.009	1.855	8.854
1.40	-262.1	0.007	1.790	9.042
1.50	-270.6	0.007	1.726	9.186
1.60	-278.0	0.003	1.661	9.311
1.70	-282.2	0.004	1.599	9.413
1.80	-289.9	0.004	1.536	9.512
1.90	-295.2	0.005	1.474	9.602
2.00	-300.2	0.007	1.413	9.686
2.10	-305.2	0.004	1.350	9.771
2.20	-310.0	0.003	1.288	9.852
2.30	-314.7	0.001	1.226	9.931
2.40	-319.3	0.000	1.165	10.009
2.50	-323.9	-0.003	1.104	10.087
2.60	-328.3	-0.003	1.045	10.161
2.70	-332.5	-0.001	0.989	10.232
2.80	-336.3	0.008	0.939	10.296
2.90	-340.7	0.002	0.880	10.371
3.00	-344.7	0.003	0.827	10.438
3.10	-348.6	0.004	0.775	10.504
3.20	-353.5	0.002	0.724	10.570
3.30	-356.4	-0.001	0.674	10.636
3.40	-360.2	-0.006	0.625	10.700
3.50	-363.5	0.000	0.583	10.756
3.60	-366.8	0.003	0.543	10.813
3.70	-370.0	0.007	0.505	10.866
3.80	-373.1	0.011	0.469	10.919
3.90	-376.1	0.015	0.435	10.969
4.00	-379.0	0.019	0.404	11.018

checked this value with an LKB 8700-1 reaction calorimeter, which had been calibrated by measuring the heat of solution of solid tham in an excess of 0.1M-hydrochloric acid. The value found for the latter reaction (7.099 kcal. mole⁻¹) is in good agreement with the literature value.⁹ The heat of protonation for tham was found to be 11.266 ± 0.004 kcal. mole⁻¹ with the LKB 8700-1 instrument, virtually the same, within experimental error, as that found with the titration calorimeter.

For the protonation measurements, different volumes of a standard solution of nitric acid were added to ca. 90 ml. of a 0.5M-potassium nitrate solution containing 2—2.5 mmoles

RESULTS AND DISCUSSION

Table 3 shows the values of $\log K$, ΔH , and ΔS for the two successive stages of protonation and for the overall reaction.

Basicity Constants.—The basicity constant of the first amino-group increases steadily from a value of 9.98 for ethylenediamine to 11.02 for hexamethylenediamine and tends to a limiting value. The biggest change occurs between ethylenediamine and trimethylenediamine. The same trend, but much more marked, is found for the basicity of the second amino-group which varies from 7.28 for the first to 10.24 for the last member of the series. However, it is well known that in primary n-alkylamines the basicity constant does not increase with chain length but only shows a small fluctuation about a fixed value. This would indicate, as was recognized by Clark and Perrin,² that the addition of a methylene group has a negligible effect on the basicity. Thus it is clear that the increasing value of $\log K$ for the diamine series must be due to the increasing distance of the other NH₂ or NH₃⁺ substituent from the basic centre being studied; both these substituents would decrease the basicity of that centre.

Enthalpy Changes.—Table 3 shows that $-\Delta H$ increases regularly from ethylenediamine to hexamethylenediamine for both the first and second stages of protonation. A gradual increase of $-\Delta H$ with increasing alkyl chain length is also observed for monoamines.³ However, for the monoamines, the change in $T\Delta S$ compensates almost entirely for this increase so that ΔG remains practically constant. In the diamine series, however, the variation in $T\Delta S$ is not sufficient to compensate completely for the increase in $-\Delta H$. Thus we conclude that the increase in basicity is mainly due to the enthalpy term. Hence, though the addition of a methylene group does not modify the basicity of an amine, it does lead to an increase in its enthalpy of protonation.

Calculated ΔH .—The first enthalpy of protonation of ethylenediamine is lower than that of ethylamine;³ that of trimethylenediamine is lower than that of propylamine,³ and so on. This shows that the addition of the amino-substituent causes a decrease in the enthalpy of protonation. For the first four diamines from ethylenediamine to tetramethylenediamine the second enthalpy term is lower than the first. Thus an NH₃⁺ group causes a bigger reduction in the enthalpy of

⁷ J. O. Hill, G. Öjelund, and I. Wadso, *J. Chem. Thermodynamics*, 1969, **1**, 111.

⁸ I. Wadso and R. J. Irving, *Acta Chem. Scand.*, 1964, **18**, 195; S. R. Gunn, *J. Phys. Chem.*, 1965, **69**, 2902.

TABLE 2
Calorimetric results

Amine	Calorimetric ampoule			Hydrochloric acid added		Q^a (corr.) (cal.)
	HCl (mmoles)	Amine (mmoles)	Vol. (ml.)	Vol. (ml.)	mmoles	
tn	1.1312	0.9951	95.84	2.00	0.5656	7.173
	0.5656	1.0184	92.41	2.00	0.5656	7.372
	1.1312	1.0184	94.41	2.00	0.5656	7.159
	0.0000	1.0070	93.65	2.00	0.5656	7.439
	0.5656	1.0070	95.65	2.00	0.5656	7.363
	1.1312	1.0070	97.65	2.00	0.5656	7.172
	0.0000	1.0219	91.08	2.00	0.5656	7.365
	0.5656	1.0219	93.08	2.00	0.5656	7.332
	1.1312	1.0219	95.08	2.00	0.5656	7.183
	0.0000	1.3037	90.28	2.89	0.8257	11.120
put	0.8257	1.3037	93.17	2.10	0.5999	8.020
	1.4256	1.3037	95.27	2.50	0.7143	9.480
	0.0000	1.4676	89.44	2.55	0.7142	9.660
	0.7142	1.4676	91.99	2.58	0.7514	10.100
	1.4656	1.4676	94.57	2.61	0.8457	9.900
cad	0.0000	1.3910	90.85	2.50	0.7142	9.750
	0.7142	1.3910	93.35	2.50	0.7142	9.760
	1.4284	1.3910	95.85	2.50	0.7142	9.680
	0.0000	1.2580	90.71	2.50	0.7142	9.710
	0.7142	1.2580	93.21	2.50	0.7142	9.750
hen	1.4284	1.2580	95.71	2.50	0.7142	9.630
	0.0000	1.2723	91.37	3.60	1.0188	14.064
	1.0188	1.2723	94.97	3.60	1.0188	14.135
	0.0000	1.1500	88.34	3.60	1.0188	14.076
	1.0188	1.1500	91.94	3.60	1.0188	14.105
hen	0.0000	1.2025	90.33	3.60	1.0188	14.034
	1.0188	1.2025	93.93	3.60	1.0188	14.091

* Corrected for heats of dilution.

TABLE 3
Thermodynamic functions of protonation in 0.5M-potassium nitrate at 25° a

Reaction	$\log K$ (mole ⁻¹ l.)	$-\Delta H^\circ$ (kcal. mole ⁻¹)	ΔS° (cal. deg. ⁻¹ mole ⁻¹)	ΔS° b corrected for statistical effect
en + H ⁺ \rightleftharpoons enH ⁺	9.98 c \pm 0.01	12.18 c \pm 0.06	4.8 c \pm 0.2	3.4
enH ⁺ + H ⁺ \rightleftharpoons enH ₂ ²⁺	7.28 c \pm 0.01	10.90 c \pm 0.14	-3.3 c \pm 0.5	-1.9
en + 2H ⁺ \rightleftharpoons enH ₂ ²⁺	17.26 c \pm 0.08	23.08 c \pm 0.08	1.5 c \pm 0.3	
tn + H ⁺ \rightleftharpoons tnH ⁺	10.55 c \pm 0.01	13.09 \pm 0.06	4.4 \pm 0.2	3.0
tnH ⁺ + H ⁺ \rightleftharpoons tnH ₂ ²⁺	8.88 c \pm 0.02	12.63 \pm 0.14	-1.9 \pm 0.5	-0.5
tn + 2H ⁺ \rightleftharpoons tnH ₂ ²⁺	19.43 c \pm 0.01	25.76 \pm 0.08	2.5 \pm 0.3	
put + H ⁺ \rightleftharpoons putH ⁺	10.804 \pm 0.002	13.58 \pm 0.06	3.9 \pm 0.2	2.5
putH ⁺ + H ⁺ \rightleftharpoons putH ₂ ²⁺	9.634 \pm 0.003	13.16 \pm 0.12	-0.1 \pm 0.4	1.3
put + 2H ⁺ \rightleftharpoons putH ₂ ²⁺	20.438 \pm 0.001	26.74 \pm 0.06	3.8 \pm 0.2	
cad + H ⁺ \rightleftharpoons cadH ⁺	10.916 \pm 0.004	13.86 \pm 0.08	3.5 \pm 0.3	2.1
cadH ⁺ + H ⁺ \rightleftharpoons cadH ₂ ²⁺	10.050 \pm 0.008	13.41 \pm 0.14	0.9 \pm 0.5	2.3
cad + 2H ⁺ \rightleftharpoons cadH ₂ ²⁺	20.966 \pm 0.004	27.27 \pm 0.06	4.4 \pm 0.2	
hen + H ⁺ \rightleftharpoons henH ⁺	11.024 \pm 0.004	13.91 \pm 0.06	3.8 \pm 0.2	2.4
henH ⁺ + H ⁺ \rightleftharpoons henH ₂ ²⁺	10.242 \pm 0.008	13.71 \pm 0.10	1.0 \pm 0.4	2.4
hen + 2H ⁺ \rightleftharpoons henH ₂ ²⁺	21.266 \pm 0.004	27.62 \pm 0.04	4.8 \pm 0.2	

* Uncertainty intervals associated with all values are twice the standard deviations. b Expressed in cal. deg.⁻¹ mole⁻¹. c Values obtained from ref. 5.

protonation than an NH₂ group. Clearly this effect decreases with increasing chain length but it only becomes negligible for hexamethylenediamine, for which the two enthalpies of protonation are equal, within experimental error, and are the same as that for butylamine.³ On this basis, we have attempted to find an empirical formula which would enable the enthalpy of protonation of any primary amino-group to be calculated. For this purpose we have also considered a series of

monoamines (see Table 4) for which reliable values of ΔH were available.^{3,10} The formula is shown in equation (1):

$$-\Delta H = \Delta H(\text{NH}_2) + a\delta(C) + b\delta(\text{NH}_2) + c\delta(\text{NH}_3^+) \quad (1)$$

where $a = \Sigma(1/2)^{n-1}$ the sum being over all carbon atoms; $b = (1/2)^{n-1}$; $c = (1/2)^{n-1}$; n is the position of the atom concerned (carbon or nitrogen) with respect to the amino-group being protonated. $\Delta H(\text{NH}_2) = 12.66$ kcal. mole⁻¹, the enthalpy of protonation of an NH₂

¹⁰ G. Öjelund and I. Wadso, *Acta Chem., Scand.*, 1968, **22**, 2691.

group. $\delta(C) = 0.66$ kcal. mole $^{-1}$, the effect of the carbon in position 1 on the enthalpy of protonation. $\delta(NH_2) = -5.78$ kcal. mole $^{-1}$, the effect of the NH_2 group in position 1 on the enthalpy of protonation. $\delta(NH_3^+) = -10.83$ kcal. mole $^{-1}$, the effect of the NH_3^+ group in position 1 on the enthalpy of protonation.

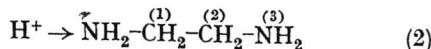
TABLE 4

Reaction	$-\Delta H^\circ_{\text{exp.}}$ (kcal. mole $^{-1}$)	$-\Delta H^\circ_{\text{calc.}}$ (kcal. mole $^{-1}$)	Residuals (kcal. mole $^{-1}$)
MeNH ₂ + H ⁺	13.29 ^a	13.32	-0.03
EtNH ₂ + H ⁺	13.71 ^a	13.65	0.06
Pr ^a NH ₂ + H ⁺	13.80 ^b	13.81	-0.01
Pr ^b NH ₂ + H ⁺	13.92 ^b	13.98	-0.06
Bu ^a NH ₂ + H ⁺	13.98 ^a	13.90	0.08
Bu ^a NH ₂ + H ⁺	13.92 ^a	13.98	-0.06
Bu ^a NH ₂ + H ⁺	14.03 ^a	14.14	-0.11
Bu ^b NH ₂ + H ⁺	14.38 ^b	14.31	0.07
n-Pentyl NH ₂ + H ⁺	13.98	13.94	0.04
i-Pentyl NH ₂ + H ⁺	14.03 ^a	13.98	0.05
en + H ⁺	12.18 ^c	12.21	-0.03
enH ⁺ + H ⁺	10.90 ^c	10.94	-0.04
tn + H ⁺	13.09	13.09	0.00
tnH ⁺ + H ⁺	12.63	12.46	0.17
put + H ⁺	13.58	13.54	0.04
putH ⁺ + H ⁺	13.16	13.22	-0.06
cad + H ⁺	13.86	13.76	0.10
cadH ⁺ + H ⁺	13.41	13.60	-0.19
hen + H ⁺	13.91	13.87	0.04
henH ⁺ + H ⁺	13.71	13.79	-0.08

$$U = \Sigma(\text{residuals})^2 = 0.13$$

^a Ref. 3. ^b Ref. 10. ^c Ref. 5.

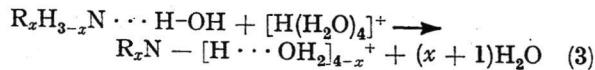
The values shown in Table 4 were calculated by least-squares. For example, for the first enthalpy of protonation of ethylenediamine [reaction (2)], $-\Delta H_1 =$



$12.66 + (1 + 1/2)0.66 - (1/4)5.78 = 12.21$ kcal. mole $^{-1}$. The calculated values for all the amines considered are shown in Table 4, column 2. The difference between the experimental and calculated values never exceeds 0.19 kcal. mole $^{-1}$. The effect produced by a carbon atom in α -, β -, and γ -positions calculated from Christensen's formula³ (0.38, 0.14, and 0.11 kcal. mole $^{-1}$) is very close to that found by us (0.33, 0.17, and 0.08 kcal. mole $^{-1}$). Satisfactory results were obtained for a series of dialkylamines with a value of 10.8 kcal. mole $^{-1}$ for $\Delta H(NH)$. However, the calculation of the first enthalpy of protonation of hydrazine with our formula gives 6.89 kcal. mole $^{-1}$, which is appreciably lower than the experimental value of 9.97 kcal. mole $^{-1}$. For this compound the agreement between the experimental and calculated values improves markedly if a factor of 1/1.5 instead of 1/2 is used in the formula. Then we obtain the following values: $\Delta H(NH_2) = 12.70$ kcal. mole $^{-1}$, $\delta(C) = 0.54$ kcal. mole $^{-1}$, $\delta(NH_2) = -2.83$ kcal. mole $^{-1}$, and $\delta(NH_3^+) = -5.30$ kcal. mole $^{-1}$. However, with these values the agreement is much poorer for nearly all the other amines considered; the residual is 0.47 instead of 0.13 (Table 4). The experimental value for the second

enthalpy of protonation of hydrazine is too inaccurate for meaningful comparison.³

Entropy Changes.—The entropy change for the first stage of protonation is always positive and decreases slightly with chain length (Table 3) from a maximum value of 4.8 cal. deg. $^{-1}$ mole $^{-1}$ for ethylenediamine. The same trend was also found for the monoamines (the values of ΔS vary from 4.1 for methylamine to 1.8 cal. deg. $^{-1}$ mole $^{-1}$ for pentylamine).³ It has previously been observed¹¹ that the entropies of protonation of alkylamines increase in the order $RNH_2 < R_2NH < R_3N$. For the same alkyl group there is an almost constant increase (5 cal. deg. $^{-1}$ mole $^{-1}$) in passing from one type to the next. In the vapour state the entropy of protonation should be negative. The fact that in aqueous solution, on the other hand, protonation is accompanied by an increase in entropy is usually explained by supposing that the reaction proceeds with the liberation of several molecules of water. Let us suppose that, to a first approximation, interaction between the amino-nitrogen and the water molecules only occurs through the nitrogen lone pair. This would mean that the number of water molecules bound by hydrogen bonding to the nitrogen atom should be the same for all primary, secondary, and tertiary amines. On the other hand, the ammonium ion can only be bound to water molecules through its positively charged hydrogen atoms. This indicates that the number of water molecules bound to an ammonium ion should be proportional to the number of hydrogen atoms which it retains, according to process (3). $x = 0, 1, 2$, or 3.



The loss of a hydrogen atom leads to the liberation of water molecules equivalent to an increment of *ca.* 5 cal. deg. $^{-1}$ mole $^{-1}$. With ethylenediamine the observed value of ΔS_1 agrees with this. An increase in the aliphatic chain length, however, leads to a slight decrease in the value of ΔS . We do not think that this variation is due to a difference in the amount of dehydration accompanying protonation, since it would logically be expected that the effect of chain lengthening on the degree of hydration of the nitrogen atom would be the same for the amino-group as for the corresponding ammonium ion. The chain-stiffening¹² of the hydrocarbon chain caused by the presence of a charge, which would naturally increase with chain length, might cause the slight decrease. Unlike ΔS_1 , ΔS_2 increases with chain length and the increase is sufficient to compensate for the decrease in ΔS_1 , so that the total ΔS increases but levels off. This increase in ΔS_2 can be explained by the chain-stiffening of the aliphatic chain caused by the repulsion between the two positive poles at the ends of the chain. Such a stiffening leads to a decrease in the entropy value and is maximum in ethylenediamine

¹¹ P. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, 1965, **69**, 3759.

¹² D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc.*, 1952, **A**, 215, 416.

where the NH_3^+ groups are nearest. This effect diminishes with increasing distance between the two poles but only disappears completely with hexamethylenediamine. For the latter, each of the two groups may be protonated without the other exerting any significant influence. This is confirmed by the fact that the two ΔS values, corrected for the statistical

effect, are essentially identical (Table 4). Furthermore, the common value of 2.4 e.u. is very close to the limiting value to which the entropies of protonation of the monoamines tend.

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Structure and Formation of Dichloro(benzylacetophenone)bis(dimethylsulphoxide)iridium(III)

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Crystals of $[\text{Ir}(\text{C}_{15}\text{H}_{13}\text{O})\text{Cl}_2(\text{Me}_2\text{SO})_2]$ are triclinic with $a = 7.471$, $b = 11.505$, $c = 13.609 \text{ \AA}$, $\alpha = 101.45$, $\beta = 107.98$, $\gamma = 89.90^\circ$, $Z = 2$, space group $P\bar{1}$. Least-squares refinement of atomic positional and vibrational parameters has been based on diffraction intensities of 2301 independent reflexions measured on a PAILRED diffractometer; the final unweighted discrepancy index is 0.073. The iridium has a distorted octahedral co-ordination made up of two dimethylsulphoxide molecules co-ordinated through their sulphur atoms [$\text{Ir}-\text{S} 2.229(7)$ and $2.243(7) \text{ \AA}$], two chloride ions [$\text{Ir}-\text{Cl} 2.376(9)$ and $2.496(9) \text{ \AA}$] and a benzylacetophenone ring forming a puckered five-membered chelate ring [$\text{Ir}-\text{O} 2.09(2) \text{ \AA}$ and $\text{Ir}-\text{C} 2.16(2) \text{ \AA}$]. Those bond lengths are discussed in detail with particular reference to the *trans*-influence of ligands in octahedral complexes. The geometry of the chelate ring strongly suggests that the complex has been formed by a Markownikoff addition reaction and this is discussed in relation to other catalytic processes.

THE catalytic action of certain iridium complexes in reducing cyclohexanones to axial alcohols and hydrogenating unsaturated ketones has been reported.^{1,2} The isolation of an intermediate in the catalysis² led us to examine its structure by X-ray methods with a view to commenting on the mechanism of catalysis.

EXPERIMENTAL

The pale yellow crystals of acicular habit were grown from benzene.

Crystal Data.— $\text{C}_{19}\text{H}_{25}\text{O}_3\text{Cl}_2\text{S}_2\text{Ir}$, $M = 628.6$, Triclinic, $a = 7.471(5)$, $b = 11.505(7)$, $c = 13.609(8) \text{ \AA}$, $\alpha = 101.45(10)$, $\beta = 107.98(9)$, $\gamma = 89.90(9)^\circ$, $U = 1088.7 \text{ \AA}^3$, $D_c = 1.92$, $Z = 2$, D_m (by flotation in benzene-dibromomethane) = 1.89, $F(000) = 612$. Space group $P\bar{1}$. Cell data from Mo- K_α precession photographs, $\lambda = 0.7107 \text{ \AA}$.

Intensity data for reflexions with $2\theta \leq 60^\circ$ were collected on a PAILRED diffractometer, using the usual moving-crystal-stationary-counter method. A $0.40 \times 0.30 \times 0.30$ mm. crystal was aligned with its a axis along the ω axis of the instrument and the reciprocal lattice layers $0-8kl$ were systematically surveyed (Mo- K_α radiation; silicon crystal monochromator). Reflexions whose independently measured background intensities differed significantly ($\geq 3.0\sigma$) or which had $F_0^2/\sigma(F_0^2) \leq 3.0$ were not incorporated in the final data set which comprised of 2301 independent reflexions having a stochastic discrepancy index of 0.063.

A distorted octahedral co-ordination of the iridium atom was immediately obvious from the three-dimensional Patterson series and a difference Fourier synthesis phased by these seven atoms gave the positions of the remaining

* Here, as elsewhere in this paper, the figure in parentheses refers to the standard deviation of the adjacent parameter.

carbon atoms; three cycles of least-squares refinement of positional and isotropic thermal parameters with unit weights reduced the unweighted R to 0.10. The introduction of anisotropic thermal vibrations for the iridium, chlorine, and sulphur atoms further reduced R to 0.081 after seven cycles of least-squares analysis. At this point a computer program for absorption correction became available and four cycles of refinement of this corrected data converged at $R = 0.074$. Attempts to refine anisotropic thermal motions of the carbon and oxygen atoms were not successful and final convergence of the least squares refinement of positional, anisotropic (iridium, chlorine, and sulphur) and isotropic (carbon and oxygen) thermal parameters was at $R = 0.073$. Final atomic parameters and their estimated standard deviations are listed in Tables 1 and 2 while structure factors are given in Table 3; atom labelling is shown in the Figure. Table 4 (a and b) summarises intramolecular bond lengths and bond angles, a number of which are also shown in the Figure.

DISCUSSION

The Molecular Structure.—The Figure shows the iridium ion to have a distorted octahedral co-ordination; the benzylacetophenone ligand forms a puckered five-membered chelate ring, two chlorine atoms are in *cis*-positions, while the remaining co-ordination sites are occupied by sulphur-co-ordinated dimethylsulphoxide (DMSO) ligands.

The major reason for distortions in the co-ordination sphere is the steric requirement of the benzylacetophenone chelate ring. As well as the angle O(1)-Ir-C(1)

¹ Y. M. Y. Haddad, H. B. Henbest, J. Husbands, and T. R. B. Mitchell, *Proc. Chem. Soc.*, 1963, 361.

² J. Trocha-Grimshaw and H. B. Henbest, *Chem. Comm.*, 1967, 544.