Thermodynamics of the Interactions of Catechol with Transition Metals. Part I. Free Energy, Enthalpy, and Entropy Changes for the Ionisation of Catechol at 25 °C. Comparison of the Temperature-coefficient Method with Direct Calorimetry

By **R. F. Jameson** * and **M. F. Wilson**, The Chemistry Department, The University, Dundee DD1 4HN

A detailed potentiometric and calorimetric study of the first proton ionisation of catechol has been made. Dissociation constants for the ionisation were determined in the temperature range 15—45 °C, and the range of ionic strength 0·060—0·180M, with KNO_3 as ionic background. Thermodynamic quantities have been calculated and values of ΔH for the ionisation have been determined both by the temperature-coefficient method and also by direct calorimetry. The results were in good agreement. An approximate value of ΔH for the second proton ionisation has also been determined by potentiometry.

ALTHOUGH the ionisation and metal-complex formation of catechol have been studied extensively by potentiometric and spectroscopic methods,[1] no reliable determination of enthalpy and entropy changes for these equilibria has been made. One of our aims was to study the effect of changing ionic medium and temperature upon the first proton ionisation in order that thermodynamic quantities could be determined at infinite dilution by extrapolation of the dissociation constants. Such values could then be compared with those determined under different conditions. In this work only the enthalpy change for the first proton ionisation of catechol could be determined calorimetrically since oxidation of the catecholate ion interfered in the determination of the second enthalpy change.

EXPERIMENTAL

Apparatus and Techniques.—The potentiometric assembly, treatment and calibration of glass electrodes, and preparation of silver–silver chloride electrodes have been described.[2] Catechol solutions were made up in dilute nitric acid, and ionic strengths were adjusted with KNO_3. The pH-meter and electrode system were standardised internally from the known initial nitric acid concentrations. Solutions were titrated with aqueous KOH solution containing added KNO_3 and of the same overall ionic strength. The pcH scale was used to record readings of hydrogen-ion concentration.[2]

---

[1] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal-ion Complexes,' *Chem. Soc. Special Publ.*, No. 17, 1964.

[2] R. F. Jameson and M. F. Wilson, preceding paper.

The LKB 8700 Precision Calorimeter used was tested by Irving and Wadsö's method [3] of measuring the heat of reaction of solid tris(hydroxymethyl)aminomethane (tham) with an excess of aqueous 0·1M-hydrochloric acid. An ampoule-breaking technique was used. Values of ΔH obtained (29·79, 29·78, and 29·74 kJ mol^{-1}; mean 29·77 ± 0·02) are in good agreement with previous values [3-7] indicating satisfactory working of the calorimeter.

Since oxidation occurs in aqueous solutions of catechol above pcH 8, measurements of the heat of neutralisation of catechol were made by the use of a batch method (a titration technique introduced a time lag during which extensive oxidation occurred). Determinations were carried out by breaking an ampoule of KOH solution into catechol solution (100 cm^3) made up in nitric acid, and it was arranged that the final ionic strength was 0·100M with respect to KNO_3; catechol solutions were purged with oxygen-free nitrogen before use to minimise oxidation. The concentration of the neutralised species was determined by measuring the pcH of the calorimetric solution at the end of the reaction with a calibrated Radiometer GK 2025B glass–calomel combination electrode.

ΔH For the formation of water in 0·100M-KNO_3 solution was measured in a separate series of experiments. Calorimetric solutions were made up containing known concentrations of nitric acid in an ionic background of slightly less than 0·100M-KNO_3. Heats of reaction were determined by breaking an ampoule of concentrated 0·20M-KOH solution into the vessel. Since an excess of base was used in these experiments the amount of water formed was equivalent to the amount of acid used (a correction was made for the heat of dilution of the added base from experimentally determined values; the heat of dilution of the KNO_3 was found to be negligible).

Preparation and Analysis of Materials.—Catechol (B.D.H.) was triply sublimed under reduced pressure and potentiometric titrations with KOH indicated better than 99·9% purity. Solutions of nitric acid were made up from standard B.D.H. ampoules and standardised with AnalaR sodium carbonate prepared by Vogel's method.[8] Potassium hydroxide solutions were prepared by Vogel's electrolytic method [8] and standardised with nitric acid solution. AnalaR KNO_3 was used for making up solutions to the correct ionic strength.

RESULTS

Enthalpy Changes for the First Proton Ionisation by the Temperature-coefficient Method.—For each series of titrations of catechol at each of the specified temperatures and ionic strengths, the average number of protons, *g*, abstracted from the ligand was calculated by use of the appropriate value of the ionic product of water.[2] The dissociation curves were plotted and those obtained for an ionic strength of 0·100M are given in Figure 1. The dissociation constants were calculated by use of the computer programme LETAGROPVRID devised by Sillén *et al.*[9-11]

Values of the dissociation constants for the first proton ionisation of catechol at various temperatures and ionic strengths are given in Table 1 together with standard deviations obtained from the computer programme. Dissociation constants at infinite dilution were obtained by extrapolation of the results by use of the extended form of the Debye–Hückel equation (1) for the activity coefficient,

$$\log f_z = \frac{-Az^2I^{\frac{1}{2}}}{1 + BaI^{\frac{1}{2}}} + CI \qquad (1)$$

where A and B are Debye–Hückel constants, I is the ionic strength, z the ionic charge, a the mean effective diameter of the ions, and C an empirical constant. This expression has been used successfully by Bates and Acree [12] and although the equation contains two arbitrary parameters, it was possible to determine values for both of these by finding the best straight line which fitted the experimental points.

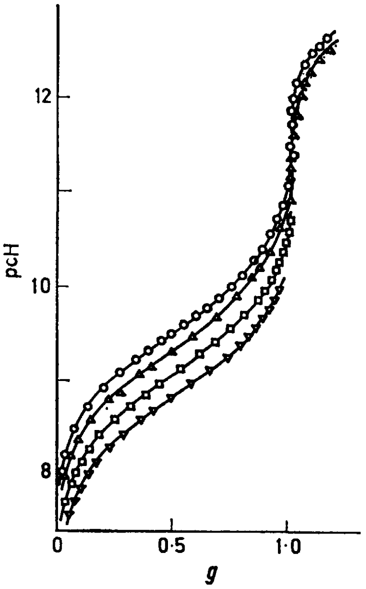

FIGURE 1 Dissociation curves for catechol ionization in aqueous 0·100M-KNO_3 at 15 (○), 25 (△), 35 (□), and 45 °C (▽)

This method of extrapolation has been used by Brannan and Nancollas.[13] Since the dissociation constant K_1^a is related to the thermodynamic dissociation constant at infinite dilution $^TK_1^a$ by expression (2), where HA represents undissociated catechol and f_x the activity coefficient of species x, then substitution of equation (1) gives, for a single ionisation, equation (3) and hence (4). The extrapolation was

$$^TK_1^a = K_1^a \cdot \frac{f_H f_A}{f_{HA}} \qquad (2)$$

$$\log {}^TK_1^a = \log K_1^a - \frac{2AI^{\frac{1}{2}}}{1 + BaI^{\frac{1}{2}}} + 2CI \qquad (3)$$

$$\log K_1^a - \frac{2AI^{\frac{1}{2}}}{1 + BaI^{\frac{1}{2}}} = \log {}^TK_1^a - 2CI \qquad (4)$$

---

[3] R. J. Irving and I. Wadsö, *Acta Chem. Scand.*, 1964, **18**, 195.

[4] G. Ojelund and I. Wadsö, *Acta Chem. Scand.*, 1967, **21**, 1838.

[5] I. Wadsö, *Sci. Tools*, 1966, **13**, 33.

[6] S. R. Gunn, *J. Phys. Chem.*, 1965, **69**, 2902.

[7] J. O. Hill, G. Ojelund, and I. Wadsö, *J. Chem. Thermodynamics*, 1969, **1**, 111.

[8] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1961.

[9] L. G. Sillén, *Acta Chem. Scand.*, 1962, **16**, 159.

[10] L. G. Sillén, *Acta Chem. Scand.*, 1964, **18**, 1085.

[11] N. Ingri and L. G. Sillén, *Arkiv Kemi*, 1964, **23**, 97.

[12] R. G. Bates and S. F. Acree, *J. Res. Nat. Bur. Stand.*, 1943, **30**, 129.

[13] J. R. Brannan and G. H. Nancollas, *Trans. Faraday Soc.*, 1962, **58**, 345.

made by plotting the left-hand side of equation (4) against I for values of a between 0 and 12 Å. Figure 2 shows the plots obtained for the results determined at 25 °C. The best values of a and C were obtained by selecting the best straight line from the more linear members of the resulting series of converging curves. Values so obtained, $a = 8{\cdot}0$ Å and $C = 0{\cdot}050$, were found to be reasonably constant over the whole temperature range. Figure 3 shows the extrapolations obtained for the four temperatures and values obtained for the dissociation constants at infinite dilution are in Table 1.

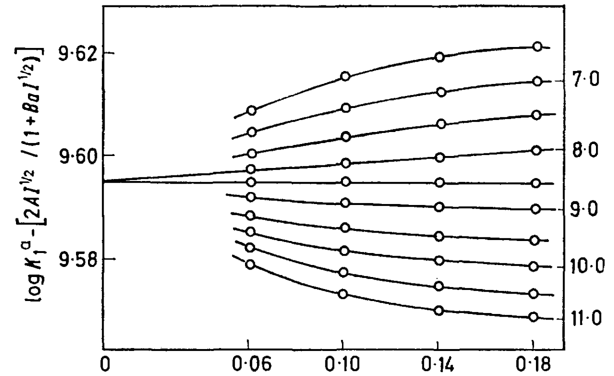

FIGURE 2 Plots of log $K_1^a - [2AI^{\frac{1}{2}}/(1 + BaI^{\frac{1}{2}})]$ against I for the first proton ionization of catechol at 25 °C, with a values of 6·5—11·0 Å

Difficulties were encountered in the investigation of the second proton ionisation since it occurs at high pcH and it was difficult to determine the dissociation constant in 0·100M-KNO$_3$ solution. In order to obtain accurate values at 15 and 25 °C, solutions of catechol were titrated with 0·100M-KOH solution; hence the ionic strength did not exceed 0·100M. It was not possible to determine pK_2^a values at the higher temperatures owing to rapid attack of the glass electrode membrane by alkali at these temperatures and also contraction of the pcH scale. Hence only an approximate value of the enthalpy change could be calculated. Values of the dissociation constant for the second proton ionisation at 15 and 25 °C and ionic strength 0·100M are in Table 1.

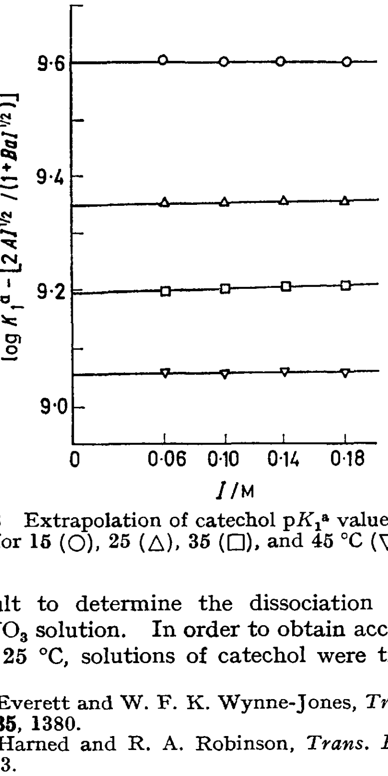

FIGURE 3 Extrapolation of catechol pK_1^a values to $I \rightarrow 0$ for 15 (○), 25 (△), 35 (□), and 45 °C (▽)

TABLE 1

Dissociation constants of catechol together with standard deviations, measured in an ionic medium of KNO$_3$

Ionic strength/ M	15 °C	25 °C	35 °C	45 °C
	pK_1^a at indicated temperatures			
→0	9·599	9·357	9·207	9·057
0·04		9·220 ±0·003		
0·06	9·450 ±0·002	9·213 ±0·002	9·050 ±0·002	8·899 ±0·002
0·10	9·430 ±0·002	9·195 ±0·002	9·039 ±0·002	8·874 ±0·002
0·14	9·414 ±0·002	9·182 ±0·002	9·023 ±0·002	8·860 ±0·002
0·18	9·405 ±0·001	9·173 ±0·002	9·015 ±0·002	8·834 ±0·002
	pK_2^a at indicated temperatures			
0·10	13·11 ±0·03	12·98 ±0·01		

The values of log K_1^a (ionic strength 0·100M) and log $^{T}K_1^a$ were fitted to three different empirical equations expressing the dissociation constant as a function of temperature, namely the Everett and Wynne-Jones equation[14] (5), the Harned and Robinson equation[15] (6), and the simple polynomial equation (7), which has been used by Feats and Ives[16] and by Nancollas.[17] The results were fitted to equations (6) and (7) by least squares by use of orthogonal polynomials,[18] and to equation (5) by the method of Everett and Wynne-Jones.[14] Values of thermodynamic quantities for catechol ionisation are given in Table 2 together with standard deviations. Since the parameters B and C in equations (5)—(7) were in this case finite, it is apparent that the relation between pK_1^a and T^{-1} is not linear and plots of this function exhibit definite curvature.

$$-\log K_1^a = \frac{A}{T} + B + C\log T \qquad (5)$$

$$-\log K_1^a = \frac{A}{T} - B + CT \qquad (6)$$

$$-\log K_1^a = A + BT + CT^2 \qquad (7)$$

Calorimetric Results for the Enthalpy Change for the Formation of Water.—Five independent determinations of the heat of formation of water, Q_W, were made and the enthalpy changes calculated. The results for the enthalpy of formation of water are: (i) in 0·100M-KNO$_3$, $\Delta H = -56{\cdot}48 \pm 0{\cdot}09$ kJ mol^{-1}; and (ii) at infinite dilution, $\Delta H^\ominus = -55{\cdot}69 \pm 0{\cdot}09$ kJ mol^{-1}. A value of the enthalpy change at ionic strength 0·100M was also calculated by the temperature-coefficient method (the Harned and Robinson

---

[14] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

[15] H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 1940, **36**, 973.

[16] F. S. Feats and D. J. G. Ives, *J. Chem. Soc.*, 1956, 2798.

[17] G. H. Nancollas, 'Interactions in Electrolyte Solutions,' Elsevier, New York, 1966.

[18] E. J. King, 'Acid–Base Equilibria,' Pergamon Press, London, 1965.

equation being applied to earlier results for the ionic product of water [2]); the value so determined was $-57{\cdot}28$ kJ mol^{-1}, slightly higher than the calorimetric value. The enthalpy change for the formation of water at infinite dilution has been examined carefully and independently by a calorimetric method by Izatt and his co-workers [19] and by Vanderzee and Swanson.[20] In both determinations it was found at infinite dilution and 25 °C to be $-55{\cdot}82$ kJ mol^{-1}, lower than the value $-56{\cdot}48$ kJ mol^{-1} determined by Harned *et al.* by the e.m.f. method.[21] Thus it is not unusual for the temperature-coefficient method to give slightly larger values of the enthalpy change for the formation of water, although the reason for this is obscure. The calculated value of the enthalpy change for the formation of water corrected to infinite dilution is $\Delta H^{\ominus} = -55{\cdot}69 \pm 0{\cdot}09$ kJ mol^{-1}. This was calculated by using known heats of dilution of KNO_3, HNO_3, and KOH obtained from tables;[22] the mean value is in good agreement with the most recently determined values.[19,20]

TABLE 2

Thermodynamic quantities for the ionisation of catechol at 25 °C with standard deviations. $I = 0{\cdot}100$M (KNO_3) except where otherwise stated

Method	Equation	Thermodynamic quantities				$\Delta C_{p(1)}^{\ominus}$/ J K^{-1} mol^{-1}
e.m.f.[a]		$-\log {}^{\mathrm{T}}K_1^{\mathrm{a}}$	$\Delta G_1^{\ominus}$/kJ mol^{-1}	$\Delta H_1^{\ominus}$/kJ mol^{-1}	$\Delta S_1^{\ominus}$/J K^{-1} mol^{-1}	
	(7)			$34{\cdot}31 \pm 0{\cdot}22$	$-65{\cdot}69 \pm 0{\cdot}84$	-590 ± 33
	(6)	$9{\cdot}356 \pm 0{\cdot}002$	$53{\cdot}43 \pm 0{\cdot}04$	$34{\cdot}10 \pm 0{\cdot}22$	$-66{\cdot}12 \pm 0{\cdot}84$	-619 ± 33
	(5)			$34{\cdot}56 \pm 0{\cdot}22$	$-64{\cdot}85 \pm 0{\cdot}84$	-669 ± 33
e.m.f.		$-\log K_1^{\mathrm{a}}$	ΔG_1/kJ mol^{-1}	ΔH_1/kJ mol^{-1}	ΔS_1/J K^{-1} mol^{-1}	$\Delta C_{p(1)}$/J K^{-1} mol^{-1}
	(7)			$34{\cdot}02 \pm 0{\cdot}22$	$-61{\cdot}93 \pm 0{\cdot}84$	-367 ± 33
	(6)	$9{\cdot}195 \pm 0{\cdot}002$	$52{\cdot}48 \pm 0{\cdot}04$	$33{\cdot}85 \pm 0{\cdot}22$	$-62{\cdot}34 \pm 0{\cdot}84$	-390 ± 33
	(5)			$34{\cdot}27 \pm 0{\cdot}22$	$-61{\cdot}09 \pm 0{\cdot}84$	-418 ± 33
cal.		$-\log K_1^{\mathrm{a}}$	ΔG_1/kJ mol^{-1}	ΔH_1/kJ mol^{-1}	ΔS_1/J K^{-1} mol^{-1}	
		$9{\cdot}195 \pm 0{\cdot}002$	$52{\cdot}48 \pm 0{\cdot}04$	$34{\cdot}46 \pm 0{\cdot}09$	$-60{\cdot}26 \pm 0{\cdot}42$	
cal.		$-\log K'$ (microscopic K)	ΔG/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	
		$9{\cdot}496$	$54{\cdot}23$	$34{\cdot}46$	$-66{\cdot}12$	
e.m.f.		$-\log K_2^{\mathrm{a}}$	ΔG_2/kJ mol^{-1}	ΔH_2/kJ mol^{-1}	ΔS_2/J K^{-1} mol^{-1}	
	(6) (2nd H)	$12{\cdot}98 \pm 0{\cdot}01$	$74{\cdot}06 \pm 0{\cdot}08$	21	-176	

[a] $I \rightarrow 0$ (KNO_3 molal scale).

Calorimetric Results for the Ionisation of Catechol.—At pcH values as low as 8·8, oxidation of catechol occurs with the formation of quinones,[23] and since the heats of oxidation of these processes are large they interfere with the determination of the enthalpy change for the second proton ionisation, and hence only the first ionisation could be investigated by calorimetry.

The heat of neutralisation (8) of catechol with strong base, Q_n, was measured. The magnitude of the correction

$$H_2L(aq) + OH^-(aq) \longrightarrow HL^-(aq) + H_2O(liq) \quad (8)$$

for the heat of formation of water was dependent upon the concentration of the excess of acid in the calorimeter solution, and since the pcH was determined after reaction, the change in hydrogen-ion concentration ($\Delta[H^+]$) was known. Hence the correction for the heat of formation of water in a particular experiment was given by equation (9). The uncorrected measured heat of reaction Q_r, was then given by (10), where Q_{dil} is the heat of dilution of KOH. The

$$Q_w = \text{volume in litres} \times (\Delta[H^+]) \times 56{\cdot}48 \text{ kJ} \quad (9)$$

$$Q_r = Q_{dil} + Q_w + Q_n \quad (10)$$

concentration of ionised catechol was calculated from the final concentration of hydrogen ions and the known pK_1^{a} value. Hence the enthalpy change for the first proton neutralisation of catechol, ΔH_n, was calculated. The enthalpy change for the first proton ionisation of catechol was given by equation (11). Measurements were carried

$$\Delta H_{ion} = \Delta H_n - \Delta H_w \quad (11)$$

out over the pcH range 8·185—8·342 with catechol concentrations in the range $1{\cdot}100 \times 10^{-2}$—$1{\cdot}200 \times 10^{-2}$M and the main values are $\Delta H_n = -22{\cdot}01 \pm 0{\cdot}09$ kJ mol^{-1} and $\Delta H_{ion} = 34{\cdot}46 \pm 0{\cdot}09$ kJ mol^{-1}.

DISCUSSION

Values of thermodynamic quantities for the first proton ionisation of catechol determined by the temperature-coefficient method in 0·100M-KNO_3 solution and at 25 °C are compared in Table 2 with those determined under the same conditions by calorimetry; the results are in good agreement. It is also interesting to compare these thermodynamic quantities with those obtained in the standard state at infinite dilution; it is apparent that the effect of the ionic background upon these quantities is small.

Values of thermodynamic quantities for the second proton ionisation in catechol (determined from e.m.f. data) are also in Table 2, but these are significantly less

---

[19] J. D. Hale, R. M. Izatt, and J. J. Christensen, *J. Phys. Chem.*, 1963, **67**, 2605.

[20] C. E. Vanderzee and J. A. Swanson, *J. Phys. Chem.*, 1963, **67**, 2608.

[21] H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, 1933, **55**, 2194.

[22] F. D. Rossini *et al.*, 'Selected Values of Chemical Thermodynamic Properties,' Nat. Bur. Stand. Circ. 500, U.S. Govt. Printing Office, Washington, 1952.

[23] F. R. Hewgill, T. J. Stone, and W. A. Waters, *J. Chem. Soc.*, 1964, 408.

accurate owing to the difficulty in obtaining reliable values of pK_2^a over the temperature range.

Although no accurate determination of enthalpy changes for catechol ionisation has been made before this work, standard thermodynamic quantities for other *ortho*-substituted phenols have been determined[24-29] and it is interesting to compare them with the results for the first proton ionisation of catechol in Table 2, *i.e.*, to regard catechol as an *ortho*-substituted phenol. Values of standard thermodynamic quantities for the ionisation of some *ortho*-substituted phenols together with the values for phenol itself are given in Table **3**. The enthalpy change for the first proton ionisation of catechol is seen to be significantly larger than for any of the other compounds. However, a characteristic property of intramolecular hydrogen bonding in such compounds[30,31] is to lower the potential energy of the base relative to that of the conjugate acid, and thus enhance acid strength.

TABLE 3

Thermodynamic quantities for the ionisation of *ortho*-substituted phenols at 25 °C (extrapolated to infinite dilution on the molar concentration scale)

Compound	ΔG_{ion} kJ mol^{-1}	ΔH_{ion} kJ mol^{-1}	ΔS_{ion} J K^{-1} mol^{-1}	Ref.
Phenol	57·03	23·22	−113·4	24
o-Propylphenol *	59·95	24·43	−119·2	25
o-Cresol	58·99	23·97	−117·6	26
o-Methoxyphenol	57·03	24·02	−110·9	27
Salicylaldehyde	47·78	21·55	−87·9	28
o-Chlorophenol	48·71	17·49	−104·6	26
o-Chlorophenol *	48·37	18·70	−99·6	29
o-Nitrophenol *	41·21	18·78	−75·3	29

* Value corrected for the most recent value of the heat of formation of water.[19,20]

It is interesting that the approximate value of the enthalpy change for the second proton ionisation of catechol, namely, 21 kJ mol^{-1}, is of the same order of magnitude as that for the ionisation of phenol.

We thank the Council of Queen's College, Dundee (latterly the University of Dundee) for a Studentship (to M. F. W.) and the S.R.C. for financial assistance in respect of this and the two following papers.

[2/998 *Received, 4th May*, 1972]

---

[24] P. D. Bolton, F. M. Hall, and J. Kudrynski, *Austral. J. Chem.*, 1968, **21**, 1541.

[25] W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Phys. Chem.*, 1963, **67**, 1933.

[26] D. T. Y. Chen and K. J. Laidler, *Trans. Faraday Soc.*, 1962, **58**, 481.

[27] F. J. Millero, J. C. Ahluwalia, and L. G. Hepler, *J. Chem. and Eng. Data*, 1964, **9**, 192.

[28] F. J. Millero, J. C. Ahluwalia, and L. G. Hepler, *J. Chem. and Eng. Data*, 1964, **9**, 319.

[29] L. P. Fernandez and L. G. Hepler, *J. Amer. Chem. Soc.*, 1959, **81**, 1783.

[30] J. Corse and L. L. Ingraham, *J. Amer. Chem. Soc.*, 1951, **73**, 5706.

[31] J. Corse, L. L. Ingraham, G. F. Bailey, and F. Stitt, *J. Amer. Chem. Soc.*, 1952, **74**, 2297.