

Studies of Isotopic Exchange Reactions Between Alkali Iodides and Butyl Iodide in Acetone

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Isotopic exchange reactions between butyl iodide and alkali iodides in acetone at 25°C have been studied for various concentrations of the ionic iodide. Kinetic data have been analysed by means of the Acree equation $k = k_i\alpha + k_m(1-\alpha)$, where k is the observed second-order rate constant, k_i and k_m are rate constants for the reactions of ions and ion-pairs, respectively, and α is the degree of dissociation of the salt. The results do not indicate significant reactivity of the alkali iodide ion-pairs.

According to the Acree hypothesis k_i should be independent of the nature of the cation. The result of this research supports this assumption.

Association constants of the salts were determined by conductivity measurements. Data were analysed by means of the Fuoss-Onsager and Shedlovsky conductance equations.

A few years ago an investigation concerning the ion-pair reactivity in isotopic exchange reactions was started by Beronius.¹ Ion-pairs of lithium chloride¹ and bromide² in acetone seem to be unreactive species, whereas the more loosely bound ion-pairs of tetrabutyl ammonium chloride and bromide in this solvent³ may be kinetically active. Alkali iodides in methanol have also been studied.⁴ However, the slight association of ions into ion-pairs in this latter case makes the estimates of the ion-pair reactivities more uncertain.

The purpose of the present investigation was to examine whether alkali iodide ion-pairs are reactive in the exchange of ¹³¹I with butyl iodide in acetone.

EXPERIMENTAL

Reagents. Sodium, potassium, rubidium, and cesium iodides (Merck, *suprapur.*) were dried for 2 h at 120°C and allowed to cool in a vacuum desiccator. Potassium chloride (Merck, *suprapur.*), for calibration of conductivity cells, was dried for 2 h at 250°C and cooled as above.

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Acetone (Merck, *p.a.*) was purified according to Smith *et al.*⁵ The specific conductivity of the purified acetone varied between 1.6×10^{-8} and 2.3×10^{-8} $\text{ohm}^{-1} \text{cm}^{-1}$. The permittivity, ϵ , at 25°C was determined from several measurements using a Ferislot Type M 803 A Q-meter. The value $\epsilon = 20.57 \pm 0.01$ (standard deviation) was obtained. The literature value $\epsilon = 20.70$ ⁶ was used in calculations below. The corrected density at 25°C was $d_4^{25} = 0.78430 \pm 0.00002$ g ml^{-1} (standard deviation), determined by means of a Lipkin pycnometer.⁸ The viscosity at 25°C was determined with a KPG Ubbelohde Viscometer⁹ and found to be $\eta = 0.003038 \pm 0.000001$ (standard deviation) poise, in good agreement with the literature value,⁶ $\eta = 0.003040$ poise. The last value was used in the calculations.

The conductivity water, used in calibrating the cells, was obtained from a quartz distilling apparatus. Its specific conductance was less than 1×10^{-6} $\text{ohm}^{-1} \text{cm}^{-1}$.

Butyl iodide (Kebo, technical grade) was distilled in a column filled with copper turnings in order to remove any traces of hydrogen iodide or iodine. The purified product was stored in the dark. Its density at 25°C, corrected to vacuum, was 1.6070 g ml^{-1} .

Preparation of alkali radioiodides. Radioactive iodide, Na^{131}I , was obtained in a dilute aqueous thiosulphate solution from the Atomic Energy Establishment, Kjeller, Norway. The water was removed by dissolving the solution in methanol followed by evaporation. The active salt was then dissolved again in a suitable quantity of methanol and stored in the dark. To obtain the other alkali radioiodides from Na^{131}I the following procedure was used:

A Dowex 50 W-X8 ion exchanger was saturated with respect to the cation in question and the aqueous solution of the active sodium salt was passed through. The water in the eluate was removed as described above.

Preparation of solutions. Stock solutions and solutions for kinetic and conductivity measurements were prepared by weight. All weights were corrected to vacuum.

Kinetic procedure. The isotopic exchange reaction between organic and inorganic iodide was followed electroanalytically according to a procedure given in Refs. 10 and 11.

The performance of the electrolytic cell was the same as in Ref. 2. The cell was filled with inactive alkali iodide solution (50 ml). Between 5 and 20 μCi ^{131}I , dissolved in methanol, were transferred to a test-tube and the solvent evaporated. About 3 ml of the inactive solution were then transferred from the cell to the test-tube. After dissolving, the radioactive salt was retransferred to the cell.

The silver anode area was 0.126 cm^2 and the stirring rate 100 rpm.

The electrode reaction, $\text{Ag} + \text{I}^- \rightarrow \text{AgI} \rightarrow \sigma^-$, was investigated with respect to current efficiency. A current density of 5500 $\mu\text{A cm}^{-2}$ mM^{-1} alkali iodide was chosen in the kinetic measurements. This corresponds to a point on the plateau of the current efficiency *vs.* current density curve.

The reaction was started by adding 0.08–0.13 ml butyl iodide by means of a micro-syringe. For three systems (KI, RbI, CsI, respectively) the amount of the organic iodide was determined to within ± 0.05 mg by weighing the syringe before and after the addition on a Mettler Micro Balance, model M5. For the exchange between sodium iodide and butyl iodide, S_∞ , the specific activity at equilibrium, was measured and the amount of organic iodide calculated as described in Ref. 12. In cases where high accuracy is desired the observed S_∞ -values must be corrected for depositions during the reaction. Eqn. 23 in Ref. 13 was used for that purpose.

The electrolysis times varied from 14 to 68 s. To minimize the error in the velocity coefficient¹³ the electrolyses were performed after 2 half-lives of exchange. About 0.25 % of the ionic iodide in the reaction mixture was deposited on each electrode.

Radioactivity measurements. The beta activity of the electrodes was measured by means of a proportional counter. The activity readings were corrected for dead-time losses, background counts, and decay of ^{131}I . The standard deviation of the counting rate was reduced to ± 0.3 % or less.

Conductivity measurements. A Leeds and Northrup 4666 bridge was used for determining the conductances, Λ , of solutions of alkali iodides in acetone. The conductivity cells used have previously been described.¹⁴ The Lind-Zwolenik-Fuoss¹⁵ method was used for calibrating the cells. Four cells, three of them with constants of the order 0.07 cm^{-1} and one with a constant of the order 0.22 cm^{-1} , were used. The measurements were performed at $25.00 \pm 0.01^\circ\text{C}$. To reduce frequency dependence extrapolation to infinite frequency was made.

Table I. Equivalent conductances in acetone at 25°C.

Run A		Run B	
$c \times 10^4$ M	Λ $\text{cm}^2 \Omega^{-1} \text{equiv.}^{-1}$	$c \times 10^4$ M	Λ $\text{cm}^2 \Omega^{-1} \text{equiv.}^{-1}$
Sodium iodide			
1.1700	190.26	1.3731	188.46
1.7667	187.72	2.1830	185.75
3.0107	182.77	3.3226	181.51
3.9263	179.51	4.4325	177.80
5.1542	176.70	5.7969	174.80
6.6877	172.25	7.4338	170.61
13.996	159.74	13.904	159.59
16.364	157.26	16.866	156.78
22.766	150.51	25.182	148.34
24.596	148.59	32.616	142.80
36.066	140.88		
Potassium iodide			
0.8715	192.01	1.0554	190.48
3.6027	180.08	4.4177	177.64
5.3972	174.89	6.7519	171.67
8.8732	167.55	10.443	164.55
13.029	160.77	13.834	159.60
19.523	152.64	21.592	150.52
23.601	148.51	26.438	145.79
30.225	143.08	31.877	141.58
Rubidium iodide			
1.1079	193.41	1.2013	193.11
2.0798	188.34	1.6814	189.64
3.1475	183.94	2.5104	186.36
5.0937	177.05	3.1577	183.30
6.8369	172.17	4.3678	178.73
11.301	162.05	5.6584	175.03
16.565	154.07	11.352	161.72
18.522	151.41	15.919	154.83
22.494	146.71	16.209	154.14
28.141	141.49	21.440	147.69
		26.511	143.18
Cesium iodide			
0.7845	197.20	2.1332	188.33
1.1532	194.10	2.7877	184.51
2.0067	189.13	4.5685	177.34
2.3557	186.99	4.8625	176.17
5.7861	173.02	8.4637	165.14
9.7928	161.98	10.170	161.24
11.095	159.40	12.320	156.70
13.016	155.33	12.847	155.57
14.328	152.88	16.268	150.06
16.532	149.51		

Table 2. Second-order rate constants, k , at 25°C for exchange of ^{131}I between alkali iodides, AI and butyl iodide at different concentrations.

Expt No.	[AI] $\times 10^4$ M	[BuI] $\times 10^4$ M	k $\text{M}^{-1} \text{min}^{-1}$
Sodium iodide			
1	3.860	109.1	4.144
2	7.733	109.1	3.967
3	12.76	104.5	3.835
4	19.62	105.4	3.760
5	29.45	134.6	3.634
6	39.19	184.9	3.503
7	59.12	185.2	3.397
8	79.02	190.5	3.268
Potassium iodide			
1	0.9641	117.6	4.149
2	3.858	111.8	3.973
3	7.604	119.4	3.863
4	11.51	120.7	3.787
5	19.07	165.0	3.640
6	28.90	187.9	3.537
7	38.85	218.7	3.411
8	57.72	219.1	3.238
9	77.12	203.3	3.136
10	96.53	223.2	3.051
Rubidium iodide			
1	2.529	149.6	3.921
2	4.856	145.0	3.842
3	4.891	149.9	3.843
4	8.043	149.4	3.764
5	12.89	149.7	3.614
6	20.19	135.0	3.454
7	24.55	144.9	3.399
8	30.72	149.2	3.347
9	39.87	153.9	3.157
10	50.08	150.8	3.089
Cesium iodide			
1	1.165	141.4	4.064
2	2.222	137.6	3.968
3	4.425	144.2	3.826
4	7.338	141.8	3.704
5	9.661	158.1	3.640
6	11.73	139.4	3.603
7	16.24	155.4	3.456
8	22.33	172.9	3.356
9	29.76	176.0	3.258

RESULTS

Equivalent conductances for the four salts studied are quoted in Table 1 for various molar concentrations. Compilations of kinetic data for the four systems studied are given in Table 2. The second-order rate constant, k , is defined by the expression $k = R/bc$, in which R is the rate of exchange according to McKay,¹⁶ b the concentration of the organic iodide, and c the concentration of the inorganic iodide. Average temperature in each run has been measured (range 24.99–25.07°C). All rate constants, k , are corrected to 25.00°C according to the Arrhenius equation. In making these calculations the value of 15 kcal mol⁻¹ was used for the activation energy. All concentrations of the salts given in Table 2 are corrected for electrolyses at zero reaction time and for dilution during the addition of the organic iodide. The degree of dissociation, α , of the alkali iodide was calculated as previously described.¹ Two sets of α -values have been calculated, one using the association constant according to the Fuoss-Onsager equation¹⁷ and one using the association constant according to the Shedlovsky¹⁸ equation. In evaluating the activity coefficient in the Debye-Hückel equation, the value 20.70 was used for the permittivity of the solvent and values given in Tables 3 and 4 for the distance of closest approach of the ions in the ion-pair (\AA).

Table 3. Conductance parameters of alkali iodides in acetone at 25°C according to the Fuoss-Onsager equation of 1957.

Salt	K_A M ⁻¹	Λ_0 cm ² Ω ⁻¹ equiv. ⁻¹	$\bar{a} \times 10^8$ cm	σ_A %
NaI	124 ± 2.0	200.5 ± 0.08	5.4	0.21
KI	120 ± 2.3	200.3 ± 0.07	4.8	0.16
RbI	192 ± 1.6	204.8 ± 0.07	5.6	0.17
CsI	264 ± 1.1	207.3 ± 0.04	5.5	0.10

Table 4. Conductance parameters of alkali iodides in acetone at 25°C according to the Shedlovsky equation.

Salt	K_A M ⁻¹	Λ_0 cm ² Ω ⁻¹ equiv. ⁻¹	$\bar{a} \times 10^8$ cm ^a
NaI	155 ± 1.9	199.6 ± 0.25	3.11
KI	167 ± 1.2	199.8 ± 0.17	3.49
RbI	228 ± 1.6	204.2 ± 0.20	3.64
CsI	312 ± 1.1	207.1 ± 0.11	3.85

^a Sum of crystallographic radii.⁷

Dissociation of alkali iodides. In order to interpret the kinetic data it was necessary to know dissociation constants, K_D , of the alkali iodides in acetone. Conductivity measurements were therefore undertaken. The equipment and

technique used for determining equivalent conductance, Λ , were as outlined in the experimental section and is described in detail in Ref. 14.

Analysis by means of the Fuoss-Onsager theory. The conductance data in Table 1 were analyzed by means of the Fuoss-Onsager equation,¹⁷

$$A = A_0 - S\sqrt{c\alpha} + Ec\alpha \log c\alpha + Jc\alpha - K_A c\alpha f^2 A \quad (1)$$

where A and A_0 have their usual meanings, c is the molar salt concentration, α the degree of dissociation, and K_A the association constant. The mean activity coefficient, f , is defined by

$$\log f = - \frac{A\sqrt{c\alpha}}{1 + B\bar{a}\sqrt{c\alpha}} \quad (1:1\text{-electrolyte}) \quad (2)$$

$$A = 1.8246 \times 10^8 / (\epsilon T)^{3/2}$$

$$B = 50.29 \times 10^8 / \sqrt{\epsilon T}$$

where ϵ is the permittivity of the solvent, T the absolute temperature, and \bar{a} the ion-size parameter. The parameters S (Onsager limiting slope), E and J are defined by equations given in Ref. 3.

To obtain A_0 , K_A and \bar{a} , conductance data were fitted to eqn. (1), using an iterative method previously described.¹⁹ The relative standard deviation in A , σ_A , as well as the standard deviation of A_0 and K_A was calculated as described in Ref. 19. Points, deviating by more than three standard deviations in A , were discarded and a further curve fitting undertaken.

Analysis by means of the Shedlovsky equation. To obtain a comparison of the parameters (A_0 , K_A) derived from the Fuoss-Onsager equation, data in Table 1 were analyzed by means of the semi-empirical Shedlovsky conductance equation,¹⁸

$$\frac{1}{AS} = \frac{1}{A_0} + \frac{K_A c A S f^2}{A_0^2} \quad (3)$$

To evaluate A_0 and K_A a computer program described in Ref. 1 was used. Note that S in eqn. (3) does not have the same meaning as S in eqn. (1). For the definition of S in eqn. (3), see, for instance, Ref. 1. Calculations were performed with the aid of a CDC 3200 computer. The results are grouped together in Tables 3 and 4.

As can be seen from Table 5, values of K_A differ greatly for the two different equations. The Shedlovsky equation gives higher K_A -values (through-out). The difference can be as large as 40 % (potassium iodide). For A_0 the agreement is good.

DISCUSSION

If iodide ions as well as alkali iodide ion-pairs are reactive and the exchange is a mixed S_N1-S_N2 reaction, the total rate of exchange can be represented by the relation

$$R = k_1 b + k_i b c \alpha + k_m (1 - \alpha) b c \quad (4)$$

Table 5. Comparison of conductance parameter.

Salt	K_A M^{-1}	A_0 $cm^2 \Omega^{-1} equiv.^{-1}$	Conductance equation
NaI	124	200.5	Fuoss-Onsager
	155	199.6	Shedlovsky
KI	120	200.3	Fuoss-Onsager
	167	199.8	Shedlovsky
RbI	192	204.8	Fuoss-Onsager
	228	204.2	Shedlovsky
CsI	264	207.3	Fuoss-Onsager
	312	207.1	Shedlovsky

where k_1 is a first-order rate constant, k_i and k_m rate constants for S_N2 exchange of ions and ion-pairs, respectively, and α the degree of dissociation of the salt. For low alkali iodide concentration, when $\alpha \approx 1$, the term containing k_m in eqn. (4) may be omitted. With these conditions eqn. (4) can be written

$$R/b = k_1 + k_i \alpha \quad (5)$$

A plot of R/b vs. α should give a straight line with slope k_i and intercept k_1 . Analysis of data in Table 2 give graphs all passing through the origin, indicating no S_N1 contribution to the reaction rate. This is illustrated in Fig. 1. If, however, $k_m \neq 0$ and the concentrations are sufficiently high, the

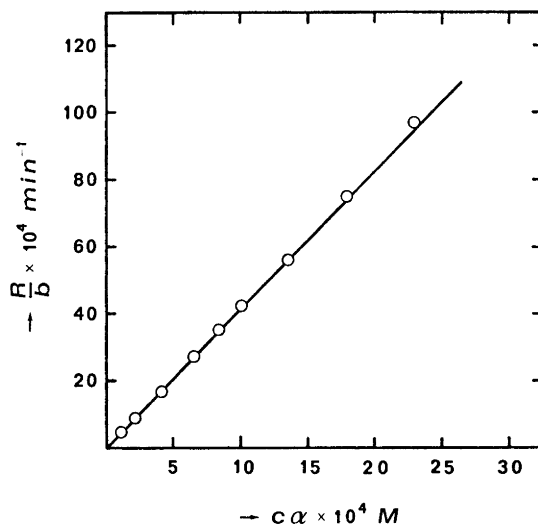


Fig. 1. Graph of R/b vs. $c\alpha$ for the exchange of ^{131}I between butyl iodide and CsI in dry acetone at $25^\circ C$ using values of α calculated according to the Fuoss-Onsager equation.

value of R depends upon the last term in eqn. (4). In this case the experimental points should deviate more and more from the limiting tangent when the concentrations of the alkali iodides increase. In Fig. 1 this behaviour is illustrated.

If $k_1 = 0$, eqn. (4) can, after rearranging, be written

$$k/\alpha = k_i + k_m(1 - \alpha)/\alpha \quad (6)$$

and becomes the Acree equation.²⁰

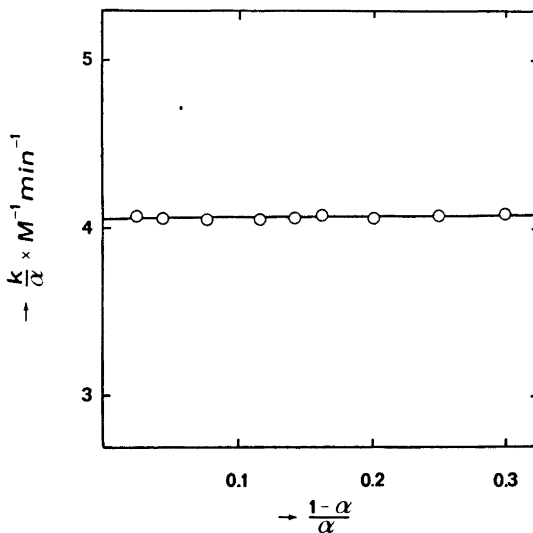


Fig. 2. Graph of k/α vs. $(1 - \alpha)/\alpha$ for the same reaction as in Fig. 1.

Table 6. Second-order specific rates, k_i and k_m , for the exchange of iodine between butyl iodide and alkali iodides in acetone at 25°C.

Salt	K_A M^{-1}	k_i $M^{-1} \text{min}^{-1}$	k_M $M^{-1} \text{min}^{-1}$	$(k_M/k_i) \times 100$ %
NaI	124 ^a	4.246 ± 0.025	-0.481 ± 0.158	-11.3 ± 3.8
	155 ^b	4.288 ± 0.022	-0.175 ± 0.124	-4.1 ± 2.9
KI	120 ^a	4.158 ± 0.013	-1.008 ± 0.081	-24.2 ± 2.0
	167 ^b	4.192 ± 0.014	-0.190 ± 0.070	-4.5 ± 1.7
RbI	192 ^a	4.099 ± 0.020	-0.164 ± 0.110	-4.0 ± 2.7
	228 ^b	4.123 ± 0.024	0.102 ± 0.118	$+2.5 \pm 2.9$
CsI	264 ^a	4.126 ± 0.015	0.272 ± 0.088	$+6.6 \pm 2.2$
	312 ^b	4.142 ± 0.013	0.547 ± 0.067	$+13.9 \pm 1.7$

^a Fuoss-Onsager conductance equation.

^b Shedlovsky conductance equation.

The method of least squares was used to evaluate k_i and k_m in eqn. (6). The results are given in Table 6. All errors are standard deviations. It can be seen from Table 6, that k_i is relatively insensitive to the choice of K_A . The

difference, for instance, in K_A for potassium iodide in acetone, according to the two conductance equations, is about 40 % but the difference in the corresponding k_i -values is less than 1 %. On the other hand, k_m is much more sensitive to the choice of K_A , as can be seen in Table 6.

From the last column in Table 6 it can be seen that most of the values in this column are negative. This "negative ion-pair reactivity" can be interpreted in terms of a kinetic salt effect.

In calculating the second-order specific rates, k_i and k_m , according to eqn. (6), these two quantities have been regarded as independent of the ionic strength. This is probably a poor assumption, particularly for k_i . Experimentally it is observed that k , which is a function of k_i , k_m , and α , decreases with increasing ionic strength (α) (see Table 2 and several examples in the literature, *e.g.*, Refs. 21–24). This change of k with concentration of the inorganic salt might be interpreted in two ways.

Firstly it may be a consequence of the increase of ionic association with increasing concentration and the different reactivities of free and paired ions. This has been discussed above. Secondly the reason may be a kinetic salt effect (changes in activity coefficients of reactants and transition-state complex). Neglect of the salt effect leads to an underestimate of the specific rate reaction of the paired ions, as has previously been pointed out.⁴ For the present, the latter effect must be neglected due to the lack of an exact correction method.

The last column in Table 6 also indicates that ion-pairs of cesium iodide may be kinetically active but the results are too uncertain to be the basis of any further conclusions. The extreme k_m -value for KI may be a consequence of a too low K_A -value.

In the derivation of eqn. (6) it is assumed that k_i is independent of the nature of the cation. This investigation supports this assumption. The deviations from average k_i -values for potassium, rubidium, and cesium iodide fall within the limits of experimental errors. For sodium iodide the deviation is greater (about 2.5 % from the average of the four k_i -values), but not great enough to infer that sodium-ion has any significance in this respect.

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REFERENCES

1. Beronius, P. *Acta Chem. Scand.* **23** (1969) 1175.
2. Beronius, P., Isacson, U. and Nilsson, A.-M. *Acta Chem. Scand.* **24** (1970) 189.
3. Beronius, P., Nilsson, A.-M. and Wikander, G. *Acta Chem. Scand.* **24** (1970) 2826.
4. Beronius, P. and Pataki, L. *J. Am. Chem. Soc.* **92** (1970) 4518.
5. Smith, S. G., Fainberg, A. H. and Winstein, S. *J. Am. Chem. Soc.* **83** (1961) 618.
6. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, p. 458.
7. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworths, London 1965, p. 461.
8. Weissberger, A., Ed., *Technique of Organic Chemistry*, 3rd Ed., Interscience, New York 1959, Vol. I, Part I, Chap. IV.
9. Weissberger, A., Ed., *Technique of Organic Chemistry*, 3rd Ed., Interscience, New York 1959, Vol. I, Part I, Chap. XII.

10. Beronius, P. *Trans. Roy. Inst. Technol. Stockholm*, No. 213 (1963).
11. Beronius, P. *Acta Chem. Scand.* **15** (1961) 1151.
12. Beronius, P. *Z. physik. Chem. (Frankfurt)* **40** (1964) 33.
13. Beronius, P. *Z. physik. Chem. (Frankfurt)* **42** (1964) 45.
14. Nilsson, A.-M., Wikander, G. and Beronius, P. *Acta Chem. Scand.* **24** (1970) 1175.
15. Lind, J. E., Zwolenik, J. J. and Fuoss, R. M. *J. Am. Chem. Soc.* **81** (1959) 1557.
16. McKay, H. A. C. *J. Am. Chem. Soc.* **65** (1943) 702.
17. Fuoss, R. M. and Onsager, L. *J. Phys. Chem.* **61** (1957) 668.
18. Fuoss, R. M. and Accascina, F. *Electrolytic Conductance*, Interscience, New York 1959, pp. 229–230.
19. Beronius, P., Wikander, G. and Nilsson, A.-M. *Z. physik. Chem. (Frankfurt)* **70** (1970) 52.
20. Acree, S. F. *Am. Chem. J.* **48** (1912) 352.
21. Evans, C. C. and Sugden, S. *J. Chem. Soc.* **1949** 270.
22. Bowers, S. D. and Sturtevant, J. M. *J. Am. Chem. Soc.* **77** (1955) 4903.
23. Lichtin, N. N. and Rao, K. N. *J. Am. Chem. Soc.* **83** (1961) 2417.
24. Bruce, W., Kahn, M. and Leary, J. A. *J. Am. Chem. Soc.* **87** (1965) 2800.

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