NOTES.

536. Physicochemical Studies on Starches. Part XIV.[1] The Effect of Acid on Wheat-starch Granules.

By A. W. ARBUCKLE and C. T. GREENWOOD.

THE effect of acid on potato-starch granules has been described in Part V.[2] During further studies of granular structure, its effect on wheat-starch granules has been investigated.

Experimental.—Wheat starch (var. Victor II) was isolated and purified as in Part XIII.[1] Methods used to treat the granules with acid in a nitrogen atmosphere, to measure the overall effect of acid-treatment on the granules, and to characterize the fractionation products were as for the previous investigation on potato starch.[2]

Initial experiments were carried out by treating the granules with 0·2M-hydrochloric acid at 45°. Potentiometric iodine titration on the products showed changes analogous to those observed for potato granules: there was an apparent increase in iodine-uptake for the first 2 hr., and a decrease thereafter. In addition, the slope of the linear portion of the curve increased with time of acid-treatment, as did the activity of free iodine necessary to

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[1] Part XIII, Arbuckle and Greenwood, preceding paper.

[2] Cowie and Greenwood, *J.*, 1957, 2658.

saturate the amylose. These results and those obtained on treating the granules with M-hydrochloric acid at 16° were as shown.

Time of acid-treatment (hr.)		0	1	2	4	6	8	24
For 0·2M-HCl at 45°	Iodine affinity	5·0	5·2	5·5	4·4	3·8	—	1·5
	Amylose (%) †	26·3	27·3	29·0	23·7	20·0	—	7·9
For M-HCl at 16°	Iodine affinity	5·0	—	5·3	5·7	—	5·6	4·8
	Amylose (%) †	26·3	—	28·0	30·0	—	29·5	25·3

† Apparent % of amylose calc. by assuming iodine affinity of amylose = 19·0 (see ref. 5).

The properties of the fractionated components from the acid-treated starches were as shown in Table 1. Degrees of polymerization ($\overline{\text{D.P.}}$) were calculated on the assumption that the relation found for potato amylose [3] holds in order to show the order of magnitude of the changes involved. Fractionation of the acid-treated starches proved more difficult than for the original starch. A similar effect was found by Kerr [4] for maize starch.

TABLE 1. *Properties of the fractionated components.*

0·2M-HCl at 45°

Acid-treatment (hr.)	Amylose			Amylopectin			
	I.A.[a]	$[\eta]$ [b]	$\overline{\text{D.P.}}$ [c]	I.A.[a]	% Amylose [d]	$[\eta]$ [b]	$10^{13} S_{20}$ [e]
0	19·0	260	1920	0·5	3	140	121
1	10·3	178	1320	—	—	80	28
2	11·2	164	1210	—	—	60	22
4	12·5	140	1030	0·5	3	—	—
6	14·8	134	990	0·8	4	50	19
24	—	—	—	—	—	30	5

M-HCl at 16°

Acid-treatment (hr.)	Amylose			Amylopectin			
	I.A.[a]	$[\eta]$ [b]	$\overline{\text{D.P.}}$ [c]	I.A.[a]	% Amylose [d]	$[\eta]$ [b]	$10^{13} S_{20}$ [e]
0	19·0	260	1920	0·5	3	140	121
2	12·6	235	1740	0·7	4	175	110
4	16·8	212	1570	1·5	8	110	80
8	18·7	188	1390	1·1	6	140	85
24	—	150	1110	0·8	4	160	56

[a] Iodine affinity (see ref. 5). [b] Measured in M-KOH. [c] Calc. from $\overline{\text{D.P.}} = 7{\cdot}4[\eta]$ (see ref. 3). [d] % of amylose impurity calc as in ref. 3. [e] Sedimentation constant in c.g.s. units at $c = 0{\cdot}2$ g./100 ml.

Discussion.—Potentiometric iodine titrations suggested that amylopectin was preferentially solubilized to give an increase in the apparent amount of linear material in the granule. The amount of reducing sugar in the acid supernatant liquid was, however, small as shown by chromatography.

The rate of degradation of the *amyloses* was expressed as (1) the number of bonds broken per initial molecule, and (2) $1/[\eta]$, both as a function of time.[2, 6] For the products isolated after treatment with 0·2M-acid at 45°, the graphs of these functions were essentially similar to those for potato, and the extrapolated curves did not pass through the origin (cf. Fig. 3 of ref. 2). The linear portion corresponded, however, to a rate of only 0·1 bond broken per initial molecule per hour, which is 4—5 times slower than that for potato. For the M-acid at 16°, degradation was limited (*ca.* 0·05), and there was no evidence of any initial preferential breakdown.

Degradation of the *amylopectins* was calculated from the plot of $1/S$ *versus* t. For the reasons already given,[2] this must be a minimum rate. The samples isolated after treatment with 0·2M-acid at 45° showed an initial preferential breakdown, which was much larger than that for amylose and may well represent attack on amylopectin in the outer surface or amorphous regions (cf. ref. 2). The linear portion of the curve corresponded to a rate of about 0·4 (same units as above), which was slower than that for potato amylopectin. At

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[3] Cowie and Greenwood, *J.*, 1957, 2862.
[4] Kerr, *Stärke*, 1952, **4**, 39.
[5] Anderson and Greenwood, *J.*, 1955, 3016.
[6] Bryce and Greenwood, *J. Polymer Sci.*, 1957, **25**, 480.

16°, the M-acid caused relatively little degradation (*i.e.*, a rate of *ca.* 0·07), although more than for the corresponding amylose, and in contrast to the results at 45° there was only limited initial preferential breakdown.

The effect of treating wheat-starch granules with 0·2M-acid at 45° could be explained by attack by acid in the manner already suggested for potato starch.[2] The calculated rates of degradation of the two components are, however, less than for potato. This may be related to a more compact structure for wheat starch, and thus an increased resistance to dispersion and fractionation.[1] The very limited accessibility of the granules is emphasized by the relatively negligible effect of M-hydrochloric acid at 16° on the molecular size of the components.

These studies suggest that there may be some fundamental difference in granular structure between tuber and cereal starches. Further methods of examining this are therefore being investigated.

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537. *Quaternary Ammonium Salts. Part V.* The Effect of Different Nucleophilic Reagents on the Mode of Decomposition of Quaternary Ammonium Salts.*

By Wadie Tadros, Alfy Badie Sakla, and Moheb Sadek Ishak.

This paper reports that the mode of decomposition of quaternary ammonium salts possessing an activating *para*-substituent in a benzene nucleus may be affected by the nature of the nucleophilic reagent used (see Table).

Salt	Reagent	Solvent	Products [a]
$CO(C_6H_4{\cdot}NMe_3I\text{-}p)_2$	OEt^- [h]	95% EtOH [b]	$CO(C_6H_4{\cdot}OEt)_2$ (50—55%); $EtO{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NMe_2$ (20—25%); Michler's ketone (5—10%); $EtO{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}OH$ (trace)
	CN^- [d]	,,	Michler's ketone; $EtO{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}NMe_2$ (trace)
	$HO{\cdot}C_2H_4{\cdot}O^-$	$(CH_2{\cdot}OH)_2$	$CO(o\text{-}C_6H_4{\cdot}C_2H_4{\cdot}OH)_2$ [c] & Michler's ketone (mainly)
$p\text{-}NC{\cdot}C_6H_4{\cdot}NMe_3Cl$	OEt^- [i]	95% EtOH [b]	$p\text{-}NMe_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ (40—45%); $p\text{-}OEt{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ (35—40%); $p\text{-}NMe_2{\cdot}C_6H_4{\cdot}CO_2H$ (a little)
$p\text{-}NO_2{\cdot}C_6H_4{\cdot}NMe_3Cl$	OEt^- [j]	EtOH	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}OEt$ [f]
	OMe^- [k]	MeOH	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}OMe$
	SCN^- [2]	MeOH	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}NMe_2$
	CN^- [d]	95% EtOH	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}NMe_2$; MeCN; $p\text{-}NO_2{\cdot}C_6H_4{\cdot}OEt$ (a little)
	$HO{\cdot}C_2H_4{\cdot}O^-$ [d]	$(CH_2{\cdot}OH)_2$	$p\text{-}NO_2{\cdot}C_6H_4{\cdot}OH$; $p\text{-}NO_2{\cdot}C_6H_4{\cdot}NMe_2$
$CHPh_2{\cdot}NMe_3Br$ (I) [g]	CN^- [d]	$(CH_2{\cdot}OH)_2$ [b]	$CHPh_2{\cdot}O{\cdot}C_2H_4{\cdot}OH$; NMe_3; $CHPh_2{\cdot}NMe_2$; MeCN

[a] The figures reported are the relative proportions of products and not the degree of decomposition. When ethyl-alcoholic solutions of these quaternary salts were boiled for 10—12 hr. there was slight decomposition in the case of benzophenone-4 : 4′-bis(trimethylammonium iodide), a trace of Michler's ketone being formed; the other salts were recovered almost without decomposition. [c] This ketone was prepared [6a] by stirring, in an autoclave for 6 hr. at 90—100°, 4 : 4′-dihydroxybenzophenone and ethylene oxide in the presence of sodium methoxide in methanol, and from 4 : 4′-dihydroxybenzophenone and ethylene bromohydrin. [d] Yields are given in the Experimental part. [e] The nitrile is hydrolysed to the amide group before degradation of the quaternary ammonium group. Decomposition of the *p*-carbamoylphenyltrimethylammonium ion thus formed gave the products mentioned in the Table. [f] Decomposition of the iodide with 95% or absolute ethanolic sodium ethoxide confirmed this finding. [g] See also Hughes and Ingold.[5] We found that the iodide had m. p. 170—175° given by them; Sommelet (*Compt. rend.*, 1922, **175**, 1149) gave m. p. 205°. [h] Tadros and Latif, *J.*, 1949, 3337. [i] Tadros and Sakla, *J.*, 1954, 1116. [j] Zaki and Fahim, *J.*, 1942, 270. [k] Bolto and Miller, *Austral. J. Chem.*, 1956, **9**, 74.

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* Part IV, *J.*, 1954, 1116.

The effect of causing the decomposition by 2-hydroxyethoxide instead of ethoxide may be related, at least in part, to a difference in electronic contribution (dipole moment [1] of ethanol, 1·691, 1·702, and of ethylene glycol, 2·28). The effect of the cyanide ion was similar to that of thiocyanate [2] on the decomposition of a trimethyl-*p*-nitrophenylammonium salt; Snyder and Speck,[3] however, report that benzyldimethylphenylammonium chloride was cleaved by boiling aqueous potassium thiocyanate solution but was unaffected under the same experimental conditions by sodium cyanide. A peculiar behaviour of the cyanide ion has been observed in other types of nucleophilic substitution.[4a] The cyanide ion in our reaction was not introduced into the benzene nucleus, although Beringer *el al.* showed that sodium cyanide reacted with 2- or 3-nitrodiphenyliodonium bromide to give the 2- or 3-nitrobenzonitrile.[4b]

EXPERIMENTAL

Diphenylmethanol, m. p. 68° [from light petroleum (b. p. 50—70°)], was obtained (*ca.* 65%) by reduction of benzophenone (200 g.) with sodium 2-hydroxyethoxide [from sodium (15·4 g.)] in ethylene glycol (330 c.c.) for 45 min. at the b. p.

Diphenylmethyl 2-Hydroxyethyl Ether.—Diphenylmethyl bromide [5] (10 g.) in ethylene glycol (30 c.c.) was warmed on the water-bath for 5 hr., then diluted with cold water (15 c.c.); the *ether*, obtained in almost quantitative yield and recrystallised from a little alcohol, had m. p. 69° (Found: C, 79·4; H, 7·0. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%).

4 : *4'-Di-(2-hydroxyethoxy)benzophenone.*—Prepared from the sodium salt of the dihydroxyketone and ethylene bromohydrin by the standard method (4·28 g. of ketone; 1·15 g. of sodium; 30 c.c. of ethanol; 1 hour's refluxing), this compound had m. p. 167—168° (from alcohol) (Found: C, 67·7; H, 5·8. Calc. for $C_{17}H_{18}O_5$: C, 67·5; H, 6·0%). Caldwell [6] gave m. p. 174°.

Decomposition of Quaternary Salts.—(A) *Decomposition with potassium cyanide.* (*a*) Trimethyl-*p*-nitrophenylammonium iodide (3·08 g.) and potassium cyanide (1·95 g.) in 95% or absolute alcohol (30 c.c.) were refluxed. The solvent and methyl cyanide (identified as acetamide, m. p. and mixed m. p. 82°) were later distilled off and the residue was washed with water and recrystallised from alcohol. The product after 6 hours' heating was *NN*-dimethyl-*p*-nitroaniline (1·12 g.), m. p. and mixed m. p. 162—163°. Dilution of the alcohol mother-liquor gave a small quantity of *p*-nitrophenetole, m. p. and mixed m. p. 56—57°.

(*b*) A similar experiment (10 hr.) with *p*-cyanophenyltrimethylammonium iodide (2·88 g.) gave mainly *p*-dimethylaminobenzonitrile (1·16 g.), m. p. and mixed m. p. 76°.

(*c*) Diphenylmethyltrimethylammonium bromide [5] (3·06 g.) or iodide (3·53 g.) and potassium cyanide (1·95 g.) in ethylene glycol (30 c.c.) were heated on the water-bath for 10 hr. Trimethylamine was formed and identified as tetramethylammonium iodide, m. p. >230° (Found: I, 62·8. Calc. for $C_4H_{12}NI$: I, 63·2%). The ethylene glycol mother-liquor was diluted with water (15 c.c.) and extracted with ether. The extract was washed with dilute hydrochloric acid and evaporated. The residue, recrystallised from little alcohol, gave diphenylmethyl 2-hydroxyethyl ether m. p. and mixed m. p. 69°. The hydrochloric acid layer was neutralised with dilute aqueous sodium hydroxide. The diphenylmethyldimethylamine precipitated formed colourless crystals, m. p. and mixed m. p. 70°, from alcohol (picrate, m. p. and mixed m. p. 196°).

(*d*) Benzophenone-4 : 4'-bis(trimethylammonium iodide) (2·76 g.) and potassium cyanide (1·95 g.) in ethanol (150 c.c.) were refluxed for 6 hr., then diluted with cold water until precipitation was complete. Michler's ketone (0·6051 g., 45·2%), m. p. and mixed m. p. 172°, was obtained on recrystallisation from alcohol. When refluxing was for 10 hr., a trace of 4-dimethylamino-4'-ethoxybenzophenone, m. p. and mixed m. p. 108°, was also obtained.

(B) *Decomposition with sodium 2-hydroxyethoxide in ethylene glycol.* (*a*) Trimethyl-*p*-nitrophenylammonium iodide (3·08 g.) and sodium (0·46 g.) dissolved in ethylene glycol (25

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[1] Conway, "Electrochemical Data," Elsevier Publ. Co., Amsterdam, 1952, pp. 14—15.

[2] Bolto and Miller, *J. Org. Chem.*, 1955, **20**, 558.

[3] Snyder and Speck, *J. Amer. Chem. Soc.*, 1939, **61**, 668.

[4] (*a*) Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 345; (*b*) Beringer, Brierley, Drexler, Cindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2708.

[5] Hughes and Ingold, *J.*, 1933, 69.

[6] Caldwell, U.S.P. (to Eastman Kodak) 2,675,411 and 2,675,367; *Chem. Abs.* 1954, **48**, 8262.

c.c.) were heated on the water-bath for 3 hr., then diluted with water, and the precipitate was treated with boiling water. The undissolved *NN*-dimethyl-*p*-nitroaniline (0·3 g.), recrystallised from alcohol, had m. p. and mixed m. p. 162—163°. The aqueous mother-liquor gave, on cooling, *p*-2-hydroxyethoxynitrobenzene (overall yield, 0·7 g.), m. p. and mixed m. p. 83—84°.

(*b*) Benzophenone-4 : 4′-bis(trimethylammonium iodide) (2·76 g.) and sodium (0·34 g.) dissolved in ethylene glycol (30 c.c.) were heated on the water-bath for 3 hr., then treated with hydrochloric acid (1 : 1), and the undissolved fraction was filtered off and recrystallised from alcohol to give 4 : 4′-di-(2-hydroxyethoxy)benzophenone (0·08 g.), m. p. and mixed m. p. 167—168°. On addition of aqueous sodium hydroxide to the acid filtrate, a small fraction, which from alcohol formed greenish-yellow crystals (0·06 g.), m. p. 128—129°, separated from the still acid medium. The acid mother-liquor was made alkaline, and Michler's ketone thus obtained recrystallised from alcohol (0·25 g.; m. p. and mixed m. p. 171°).

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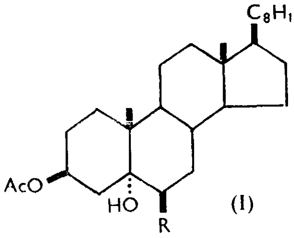
538. *A Second Carbonyl Band in the Spectra of Hydroxy-esters.*

By H. B. Henbest, G. D. Meakins, and T. I. Wrigley.

The formation of the fluorinated hydroxy-ester (I; R = F) from 3β-acetoxy-5α : 6α-epoxycholestane was reported recently.[1] The infrared spectra of solutions in CCl_4 and CS_2 of this compound and the corresponding chlorohydrin (I; R = Cl) are unusual in exhibiting two carbonyl bands, the expected acetoxyl band (1735 cm.$^{-1}$) being accompanied by a weaker band at lower frequency (1715 cm.$^{-1}$). However, in solutions of higher concentrations (see Table) the intensity of the 1715 cm.$^{-1}$ band increases while that of the 1735 cm.$^{-1}$ band decreases. The effect must thus be attributed to intermolecular association, the 1735 cm.$^{-1}$ peak representing non-associated acetoxyl (cf. the figures for 3α-acetoxycholestane) and the 1715 cm.$^{-1}$ absorption arising from acetoxyl groups involved in hydrogen-bonding between carbonyl oxygen atoms and hydroxyl groups. Although similar association is possible with 3β-acetoxycholestan-5α-ol (I; R = H) two carbonyl bands occur only at high concentration, and with the acyclic analogue, 3-acetoxypropan-1-ol, only one carbonyl band was present in the concentration range used with the steroidal hydroxy-acetates. The more pronounced tendency for bonding in the halogenohydrins is presumably due to the increased acidity of the 5-hydroxyl groups caused by inductive effects of the halogen atoms.



(I)

The hydroxyl regions of the steroidal hydroxy-acetates show non-associated and associated hydroxyl bands, the latter arising from hydroxyl–hydroxyl, hydroxyl–acetoxyl, or (less probably) hydroxyl–halogen association.[2,3] With the halogenated compounds (I; R = F and Cl) the bands of lower frequency are especially pronounced, indicating a marked contribution from the hydroxyl–acetoxyl bonding responsible for the double carbonyl absorption.

The qualitative effects of the intermolecular bonding of the halogenohydrins are similar to those already well established in spectroscopic studies of the association between hydroxyl and ester groups.[4] The unusual aspect is that the two carbonyl bands occur

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[1] Henbest and Wrigley, *J.*, 1957, 4765.

[2] Henbest and Lovell, *J.*, 1957, 1965.

[3] Nickon, *J. Amer. Chem. Soc.*, 1957, **79**, 243.

[4] Searles, Tamres, and Barrow, *ibid.*, 1953, **75**, 71, and references cited therein.

Infrared frequencies (cm.$^{-1}$) of hydroxy-esters.

The compounds were examined in CCl_4 solutions (concentrations in mole/l.) on a Perkin-Elmer Model 21 spectrometer fitted with a calcium fluoride prism. Figures in parentheses are apparent molecular extinction coefficients in mole^{-1} l. cm.$^{-1}$. The intensity ratio of a pair of bands is the intensity of the higher-frequency band divided by that of the lower-frequency component.

	C=O Region			OH Region		
	Concn.	Bands	Int. ratio	Concn.	Bands	Int. ratio
3β-Acetoxycholestane *	0·0013	1734 (570)	—			
	0·01	1735 (555)	—			
3-Acetoxypropan-1-ol	0·0013	1745 (740)	—			
	0·01	1745 (730)	—			
3β-Acetoxycholestan-5α-ol (I; R = H) *	0·0013	1737 (550)	—	0·02	3615 (35)	0·9
	0·0051	1737 (570)	—		3465 (40)	
	0·01	1737 (510)	4·5			
		1718 (115)				
3β-Acetoxy-6α-chlorocholestan-5α-ol (I; R = Cl)	0·0013	1735 (515)	4·0	0·02	3605 (35)	0·6
		1718 (130)			3445 (60)	
	0·0052	1735 (460)	2·3			
		1715 (200)				
	0·01	1735 (415)	1·7			
		1715 (250)				
3β-Acetoxy-6β-fluorocholestan-5α-ol (I; R = F)	0·0013	1735 (545)	4·1	0·02	3610 (35)	0·6
		1718 (130)			3445 (60)	
	0·0052	1735 (500)	2·7			
		1715 (185)				
	0·01	1736 (460)	1·9			
		1715 (240)				

* Figures differ slightly from, and are more accurate than, those reported previously.[2]

at concentrations frequently used in routine examination of organic compounds. Thus the frequencies and relative intensities of the bands observed with 1% solutions might at first sight be taken to indicate the presence of an acetoxyl group and a keto-group in a six-membered ring.

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539. *The Possible Instability of Solid Anhydrous Argentic Nitrate.*

By D. F. C. MORRIS.

THE recent isolation of anhydrous cupric nitrate [1] has prompted a theoretical consideration of the possible stability of a solid argentic nitrate $Ag(NO_3)_2$. Noyes and his colleagues [2] have prepared solutions which must have contained the ions of argentic nitrate, but the solid is unknown.[3]

The standard molar free energy of formation of solid argentic nitrate at 25° can be estimated. This quantity, ΔG°_{298}, is related to the standard molar enthalpy of formation ΔH°_{298} and the standard molar entropies S°_{298} by the expression

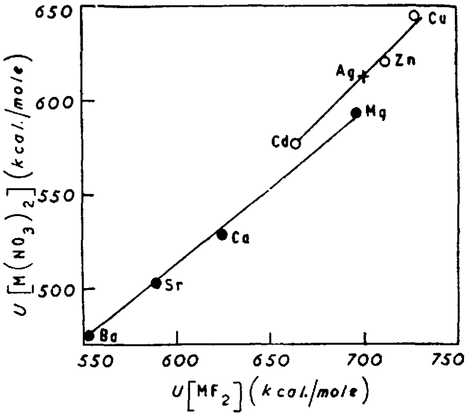
$$\Delta G^\circ_{298}[Ag(NO_3)_2\,(s)] = \Delta H^\circ_{298}[Ag(NO_3)_2\,(s)] - 298{\cdot}2\{S^\circ_{298}[Ag(NO_3)_2\,(s)] - S^\circ_{298}[Ag\,(s)] - S^\circ_{298}[N_2\,(g)] - 3S^\circ_{298}[O_2\,(g)]\} \quad . \quad . \quad (1)$$

A knowledge of requisite enthalpy and entropy data will therefore permit the evaluation of the standard free energy of formation of the solid nitrate.

The standard molar enthalpy of formation of the compound can be derived by use of the equation

$$\Delta H^\circ_{298}[Ag(NO_3)_2\,(s)] = \Delta H^\circ_{298}[M^{2+}\,(g)] + 2\Delta H^\circ_{298}[NO_3^-\,(g)] - U \quad . \quad . \quad (2)$$

where U is the lattice energy (enthalpy) of the argentic nitrate at 25°. The data necessary for the calculation of $\Delta H^\circ_{298}[Ag(NO_3)_2\,(s)]$ from equation (2) are available [4,5] except for the value of the lattice energy. Kapustinskii [6] has derived various expressions for the calculation of the lattice energies of electrovalent compounds of which the lattice constants are unknown. However, ionization potentials [7] suggest that argentic nitrate, if it existed, would have a high degree of covalent character. Therefore the use of Kapustinskii's equations does not appear to be suitable in the present case. Nevertheless, the lattice energy of $Ag(NO_3)_2$ can be estimated satisfactorily by use of various linear relations which exist between the "experimental" lattice energies of compounds of a given formula type.[8] Thus from the Figure the lattice energy of $Ag(NO_3)_2$ can be determined by interpolation, and the standard molar enthalpy of formation can then be derived.



Karapet'yants type of plot of the lattice energies of metal dinitrates and the lattice energies of corresponding difluorides.

In order to evaluate the standard free energy of formation from eqn. (1) it remains necessary to know the requisite standard entropies. These are available [4] except for $S°_{298}[Ag(NO_3)_2\ (s)]$ but this can be estimated by Latimer's method.[9]

The Table shows thermodynamic data for solid argentic nitrate and the standard enthalpy and free-energy changes for its most probable mode of decomposition. For comparison, values are quoted for solid anhydrous cupric nitrate. Where requisite data are available [4, 5] they have been used in composing the Table, otherwise magnitudes have been calculated as described here. It follows that the non-existence of a solid anhydrous argentic nitrate is in agreement with thermodynamic predictions.

Compound	$\Delta H°_{298}$ $[M^{2+}\ (g)]$ (kcal./mole)	$\Delta H°_{298}$ $[NO_3^-\ (g)]$ (kcal./mole)	U (kcal./mole)	$\Delta H°_{298}$ $[M(NO_3)_2\ (s)]$ (kcal./mole)	$S°_{298}$ $[M(NO_3)_2\ (s)]$ (e.u.)	$\Delta G°_{298}$ $[M(NO_3)_2\ (s)]$ (kcal./mole)
$Ag(NO_3)_2$ ...	740·7	−79·1	613	−31	48·2	15
$Cu(NO_3)_2$ ...	730·1	−79·1	645·3	−73·4	46·2	−27

$Ag(NO_3)_2\ (s) = AgNO_3\ (s) + NO_2\ (g) + \frac{1}{2}O_2\ (g)$; $\Delta H_{298} = 10$ kcal./mole; $\Delta G_{298} = -10$ kcal./mole; $(d\Delta G/dT)_p = -67{\cdot}4$ cal. deg.$^{-1}$.

$Cu(NO_3)_2\ (s) = CuO\ (s) + 2NO_2\ (g) + \frac{1}{2}O_2\ (g)$; $\Delta H_{298} = 53$ kcal./mole; $\Delta G_{298} = 21$ kcal./mole; $(d\Delta G/dT)_p = -104$ cal. deg.$^{-1}$.

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[*Received, February 19th*, 1958.]

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[1] Addison and Hathaway, *Proc. Chem. Soc.*, 1957, 19.

[2] Noyes, Hoard, and Pitzer, *J. Amer. Chem. Soc.*, 1935, **57**, 1221; Noyes, Pitzer, and Dunn, *ibid.*, 1229; Noyes and Kossiakoff, *ibid.*, p. 1238; Noyes, Coryell, Stitt, and Kossiakoff, *ibid.*, 1937, **59**, 1316; Noyes, De Vault, Coryell, and Deake, *ibid.*, p. 1326.

[3] Sidgwick, "The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, p. 175.

[4] Rossini, Wagman, Evans, Levine, and Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular of National Bureau of Standards, No. 500, 1952.

[5] Morris, *J. Inorg. Nuclear Chem.*, in the press.

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540. *Preparation and Some Crystallographic Properties of Triamminoacetylenemagnesium Carbide* $MgC_2{\cdot}C_2H_2{\cdot}3NH_3$.

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IN 1914 Cottrell [1] prepared a compound by the action of magnesium on acetylene dissolved in liquid ammonia. He reported that the transparent tetrahedral crystals, to which he assigned the formula $MgC_2{\cdot}C_2H_2{\cdot}5NH_3$, reversibly lost ammonia at 0—2° to give a compound, stable at room temperature, partial analysis of which indicated the formula $(MgC_2{\cdot}C_2H_2)_27NH_3$. We have repeated the preparation of the former compound and have made some crystallographic observations on it. We find its formula to be $MgC_2{\cdot}C_2H_2{\cdot}3NH_3$, but it is not certain whether the ammonia and acetylene molecules are co-ordinated to the magnesium atom.

Experimental.—Several preparations were made with different amounts of magnesium by the following method. Magnesium turnings (0·01—0·10 g.) in a Pyrex tube were outgassed by heating them *in vacuo*. The tube was cooled to $-176°$ and, after dry acetylene (0·16 g.) and then dry ammonia (0·35 g.) had been distilled in, it was sealed and allowed to warm to room temperature. After about 5 min., the solution evolved gas and deposited a white solid, which after several days at room temperature (still in the original sealed tube) was converted almost completely into transparent tetrahedral crystals, usually colourless but sometimes pale or dark brown. Unit cell dimensions of crystals of different colours were identical [Found, mean of three analyses: Mg, 19·4. Calc. for $(MgC_2{\cdot}C_2H_2)_27NH_3$: Mg, 18·1. Calc. for $MgC_2{\cdot}C_2H_2{\cdot}3NH_3$: Mg, 19·4%].

The crystals are stable in an atmosphere of dry ammonia at room temperature but with water give acetylene and magnesium hydroxide. Heating in dry ammonia gives magnesium amide which was identified by *X*-ray powder photographs. After storage *in vacuo* for 4 days, during which time the temperature rose from $-70°$ to $+20°$, the crystals had decomposed to a cream-coloured powder which did not give a satisfactory *X*-ray powder photograph; this powder contained 35·1% of magnesium so that it may be impure $MgC_2{\cdot}C_2H_2$ (cal.: Mg, 32·7%).

Single crystals were sealed into thin Pyrex capillary tubes in ammonia. They appeared isotropic under the polarising microscope and the cubic symmetry was confirmed by *X*-ray diffraction photographs. From a rotation photograph about [100] the unit cell edge was found to be $a = 16{\cdot}62 \pm 0{\cdot}02$ Å; density, found by flotation in benzene–chloroform, 1·06 g./c.c.; calculated for $24(MgC_2{\cdot}C_2H_2{\cdot}3NH_3)$, 1·09 g./c.c.; calculated for $12[(MgC_2{\cdot}C_2H_2)_27NH_3]$, 1·16 g./c.c.

X-Ray photographs taken at 20° and at $-10°$ were identical. The crystal used was in the presence of ammonia and acetylene in the sealed Pyrex tube in which it had been made, conditions in which Cottrell found a reversible absorption of ammonia. Therefore, if a change in ammonia content takes place it is unaccompanied by a detectable change in crystal lattice.

Weissenberg photographs were taken of the 0th and 1st layer about the [100] axis and the 0th, 1st, and 2nd layer about the [101] axis. The only systematic absences were those for (h00) with $h \neq 4n$ indicating that the space group is one of the enantiomorphic pair $P4_332(O^6)$ and $P4_132(O^7)$. (This is unexpected, the tetrahedral habit indicating a $\bar{4}$ axis, which would make the space group $P\bar{4}3m$ with no systematic absences.) No molecular symmetry is required by the space groups $P4_332$ or $P\bar{4}3m$, so that there are 3 parameters for each of 8 atoms (excluding hydrogen) to be determined. Unfortunately, because of the cubic symmetry and the high temperature factor the number of independent reflections (about 60) is insufficient for the determination of 24 parameters. No further work will be carried out on this compound at present.

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