

well understood that nickel(II) complexes of such strong ligands as dipyridyl dissociate only slowly in strongly acidic media. However, Ni(TRI)(H₂O)₃²⁺ appears to be much less reactive than, for example, Ni(dipy)-(H₂O)₄²⁺, for which the dissociation half-life is a few hours in the vicinity of room temperature.²² This extreme unreactivity of the complex of the cyclic tridentate ligand may be attributed to the absence of terminal donor groups in the ligand; *i.e.*, coordinated groups that might first dissociate and protonate and, in this way, initiate and perpetuate the stepwise dissociation of the ligand.

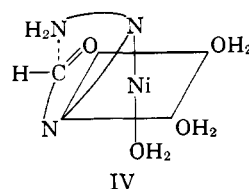
The coordinated ligand is sensitive to base. The reaction appears to involve the addition of water molecules across the Schiff base linkages to produce α -carbinolamines, in the manner observed for the similar tetradentate macrocycle.¹¹

The compounds containing the tridentate ligand and those containing the tetradentate ligand behave differently toward ethylenediamine. The addition of an aqueous solution of ethylenediamine to an aqueous solution of the nickel complex of the tetradentate ligand, Ni(TAAB)²⁺, results in the formation of the same product isolated from the reaction with hydroxide ion. However, for the tridentate derivative, Ni(TRI)(H₂O)₃²⁺ (as perchlorate), a brown solid is precipitated on the addition of an aqueous solution of ethylenediamine. The infrared spectrum of this brown solid shows the presence of ethylenediamine in addition to water and the trimeric ligand. The perchlorate anions have infrared absorptions characteristic of the ionic form. It seems most probable that an ethylenediamine molecule has displaced the anions from their *cis* positions in the coordination sphere in this product.

The mechanisms of formation of both the trimeric and tetrameric macrocycles are of considerable interest and must serve to illustrate the template influence of the metal ion.^{2, 23} The point of particular concern

(22) P. Ellis, R. Hogg, and R. G. Wilkins, *J. Chem. Soc.*, 3308 (1959).

derives from the fact that the number of *o*-amino-benzaldehyde units cyclopolymerized depends on the metal ion. In the case of copper(II) ion,¹¹ only the cyclic tetramer is generated (as its Cu(II) complex). In contrast, as shown here, the reaction with nickel(II) ion leads to both the cyclic tetramer and a cyclic trimer (as their Ni(II) complexes). Comment has been offered on the general nature of the process earlier.^{11, 23} Most reasonably it is assumed that, as the *o*-amino-benzaldehyde condenses with itself, each intermediate polymeric ligand is bound to the metal ion. The self-condensation is assumed to proceed stepwise, in this fashion, until the terminal reactive groups (an NH₂ and a CH=O group) are sufficiently close in proximity to permit final ring closure. Obviously, if a metal ion confines the donor atoms of such intermediates to an encircling plane, as in a square-planar coordination sphere, a tetrameric, tetradentate macrocycle must be produced. However, if the intermediates can bind along as many as three mutually *cis* positions (structure IV), then a trimeric, tridentate macrocycle may form. Clearly, metal ions that bind donor groups more firmly in a fourfold planar array should favor the cyclic tetramer (Cu(II)) while those of octahedral coordination spheres may produce both the tetramer and the cyclic trimer (Ni(II)).



Acknowledgment. This investigation was supported by Public Health Service Grant GM 10040 from the National Institute of General Medical Sciences.

(23) D. H. Busch, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 25, 107 (1964).

Reactions of the Uranium Carbides with Nitric Acid¹

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The uranium carbides reacted with 2 to 16 M HNO₃ at 25 to 120° yielding uranyl nitrate, soluble organic acids, NO₂, NO, and CO₂. No hydrogen, CO, or gaseous hydrocarbons were produced. Between 50 and 80% of the carbide carbon was converted to CO₂. The soluble organic species consisted of oxalic acid (0 to 11% of the carbide carbon), mellitic acid (2 to 9% of the carbide carbon), and unidentified compounds which were probably aromatics highly substituted with -COOH and -OH groups. The carbides were practically passive in boiling 0.001 to 0.5 M HNO₃.

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

Introduction

Several prior investigations of the reactions of the uranium carbides with nitric acid have been conducted, each giving somewhat different results. Simpson and Heath² studied the reaction of the monocarbide with 6 M HNO₃. Carbon-containing compounds were not found in the off-gas, so they concluded that all of the carbide carbon remained in the solution. The dark brown color of the solution was attributed to materials similar to the "humic" acids produced by oxidation of

(2) A. M. Simpson and B. A. Heath, UKAEA Report IG Memorandum 464(D), June 1959.

coal. Donaldson, *et al.*,³ reported that both the monocarbide and the dicarbide yielded mellitic (benzene hexacarboxylic) and oxalic acids in reactions with 2 to 12 *M* HNO₃, and that at least 33% of the carbide carbon was converted to CO₂ while 10% remained as a graphitic residue. Pausen, *et al.*,⁴ allowed the carbides, including the sesquicarbide, to react with 6 *M* HNO₃ and also detected mellitic and oxalic acids among the soluble species. They reported that 30 to 40% of the carbide carbon was converted to CO₂ and suggested that graphite was an intermediate in the reaction since the organic products were similar to those obtained from the oxidation of graphite or carbon. Drummond, *et al.*,⁵ noticed deposition of carbon when the uranium carbides were treated with nitric acid. Pollard, *et al.*,⁶ concluded that the reaction of uranium monocarbide with 4 *M* HNO₃ at 100° gave a gas comprised of about 65% methane, 8% hydrogen, 12% higher hydrocarbons, and 15% other gases which probably included nitrogen oxides. The present study was conducted to examine more closely the reactions of the uranium carbides with nitric acid.

Experimental

Carbides. Carbide buttons were prepared by arc melting high purity uranium metal and spectroscopic grade carbon using nonconsumable tungsten electrodes, as described previously.⁷⁻⁹ The mono- and dicarbides (UC and UC_{1.85}, respectively) were formed directly. After arc melting, specimens having C:U atom ratios of 1.5 were heat treated for 65 hr. at 1600° to form the sesquicarbide (U₄(C₂)₃).⁹ Chemical analyses of the specimens and the major components identified by X-ray diffraction analysis are given in Table I. The

Table I. Composition of Uranium Carbides

Specimen	—Analyses, wt. %—			Com- bined C:U atom ratio	—X-Ray powder— pattern ^a		
	U	Total C	Free C		UC	U ₄ - (C ₂) ₃	UC _{1.85}
ORNL-1A	95.1	4.69	0.0	0.98	S
ORNL-1B	95.3	4.64	0.02	0.96	S
ORNL-1E	96.2	4.76	0.02	0.98	S
AI-4	94.7	5.32	0.07	1.10	S	..	W
U ₂ C ₃ -1A	93.0	6.93	0.04	1.47	Q	S	Q
U ₂ C ₃ -9A	92.8	7.02	0.3	1.44	Q	S	Q
U ₂ C ₃ -13A	92.9	7.05	0.01	1.51	..	S	T
UC ₂ -16H	91.1	8.80	0.33	1.85	Q	..	S
UC ₂ -18A	90.8	9.12	0.70	1.84	Q	..	S

^a S, strong (major component); W, weak (present, but in low concentration); T, trace component; Q, questionable.

tungsten contamination from the electrodes was less than 0.2% except in specimen ORNL-1E which contained 0.2 to 0.4%. The oxygen and nitrogen con-

centrations were less than 0.1% and 80 p.p.m., respectively, with the exception of specimen U₂C₃-9A which contained about 0.3% oxygen as UO₂. Procedures for analyzing the carbides were described previously.⁷⁻⁹

Soluble Organic Products. The soluble organic products were obtained by allowing 50 to 100 g. of crushed carbide to react, using 10 ml. of nitric acid per gram of carbide. Each reaction was allowed to proceed for 24 hr., or longer if dissolution of the carbide was not complete. No attempt was made to collect or analyze the gases evolved. The acidity of the resulting solution was adjusted to about 6 *N*; then, the uranium was extracted by equilibrating the solution ten times with 20% *n*-tributyl phosphate-80% Amsco solution. Other studies¹⁰ showed that little or no extraction of the organic species occurred. The organic species were recovered as solids by evaporating the raffinate to dryness, usually under slight vacuum at room temperature.

The solid organic products were analyzed for carbon, hydrogen, and nitrogen by standard methods. Water was determined by titration with Karl Fischer reagent. Equivalent weights were determined by potentiometric titration of aqueous solutions with standard base. The carbon, hydrogen, and nitrogen analyses and the equivalent weights were corrected for the amount of water present. X-Ray powder patterns were obtained with a Debye-Scherrer 114.59-mm. diameter camera using Cu K α radiation. Patterns for several of the benzene acids were obtained from specimens prepared in this laboratory.¹¹ Infrared spectra were obtained with a Beckman IR-7 spectrometer using both the KBr pellet and methanol thin-film techniques.

Recovery of Oxalic Acid from the Organic Products. Vacuum sublimation was used to estimate both the oxalic acid and water contents of the organic products. The solids were maintained at 105 to 110° under vacuum for several hours, and the total weight loss was noted. The sublimate was dissolved in water, and the solution evaporated to dryness at room temperature. The resulting solid was shown by X-ray diffraction analysis, melting point, and titration with standard KMnO₄ solution to be pure oxalic acid dihydrate. Since no other organic compound sublimed, the difference between the total weight loss and the weight of oxalic acid was attributed to water. The water contents determined in this manner agreed well with those obtained by titration with Karl Fischer reagent.

Recovery of Mellitic Acid from the Organic Products. Samples of the solids were digested with an excess of boiling concentrated ammonium hydroxide for 16 to 20 hr. The system was then cooled to about 0° and maintained there for at least an hour; the ammonium mellitate was recovered by vacuum filtration. The ammonium mellitate was washed with cold concentrated ammonium hydroxide before being dried at 105 to 110°. Losses should have been less than 10% since the solubility of ammonium mellitate in concentrated ammonium hydroxide at 0° is only about 0.002 g./l.¹¹ In some cases, the free acid was isolated. The am-

(3) D. M. Donaldson, K. Hartley, P. Lees, and N. Parkinson, *Trans. AIME*, **227**, 191 (1963).

(4) P. L. Pausen, J. McLean, and W. J. Clelland, *Nature*, **197**, 1200 (1963).

(5) J. L. Drummond, B. J. McDonald, H. M. Ockenden, and G. A. Welch, *J. Chem. Soc.*, 4785 (1957).

(6) F. H. Pollard, G. Nickless, and S. Evered, *J. Chromatog.*, **15**, 223 (1964).

(7) M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **1**, 683 (1962).

(8) M. J. Bradley and L. M. Ferris, *ibid.*, **3**, 189 (1964).

(9) M. J. Bradley and L. M. Ferris, *ibid.*, **3**, 730 (1964).

(10) L. M. Ferris and M. J. Bradley, U. S. Atomic Energy Commission Report ORNL-3719, Dec. 1964.

(11) L. M. Ferris, *J. Chem. Eng. Data*, **9**, 387 (1964).

monium mellitate was dissolved in water, and lead acetate was added to precipitate the lead salt. After washing, the lead mellitate was slurried with water; then, H₂S was bubbled through the slurry to precipitate PbS and liberate mellitic acid (which is soluble in water). The acid was recovered from solution by evaporation and was recrystallized from 70% HNO₃. Both the ammonium mellitate and the mellitic acid were identified by X-ray diffraction analysis. The equivalent weights of the mellitic acid isolated in two experiments were 57.6 and 57.8 g./equiv., respectively, compared to a calculated value of 57.0.

Gaseous Products. In a separate series of experiments, 1- to 4-g. samples of the carbides were allowed to react with standardized nitric acid solutions at 90° and the evolved gases collected and analyzed. The procedures are described elsewhere.¹⁰ Gases were analyzed by gas chromatography using Linde 5A Molecular Sieve columns. Since NO and CH₄ could not be differentiated on this column, samples of the gases were analyzed by mass spectroscopy to ensure that NO was the component being determined. In addition, the samples were tested for C₂- to C₈-hydrocarbons with the chromatographic columns used to analyze the hydrocarbon mixtures evolved in the hydrolysis of uranium carbides.^{7-9,12} Analysis of nitrogen oxides and carbon oxides by this procedure was only semi-quantitative with an accuracy of ±30%.¹⁰ The total amount of carbon dissolved in the nitric acid-uranyl nitrate solution was determined by wet oxidation,¹³ which was accurate to ±10%.¹⁰

Results

Passivation in Dilute Nitrate Systems. All three uranium carbides were passive in boiling 0.001 to 0.5 M HNO₃ over 24-hr. periods.¹⁰ In the very dilute solutions no gas was evolved and no uranium dissolved in the nitric acid. The surfaces of the originally shiny specimens turned black, and, in some cases, the specimen crumbled to a powder. This phenomenon was not limited to nitric acid solutions; passivation also occurred in boiling sodium, calcium, uranyl, aluminum, and thorium nitrate solutions where the nitrate concentration was 0.05 M. Measurable reaction rates occurred only when the nitric acid concentration was 1 M or greater.

Gaseous Products. Dissolution of the uranium carbides in 2 to 16 M HNO₃ at 90° produced gases comprised of CO₂, NO, and NO₂.¹⁰ Traces of N₂O were found, but no CO, H₂, or hydrocarbons were detected. Between 50 and 70% of the carbide carbon was converted to CO₂. In 2 to 4 M HNO₃, NO was the main nitrogen oxide evolved, whereas NO₂ predominated at higher acid concentrations. The gas composition changed with time throughout each experiment. With UC and 2 or 4 M HNO₃, the NO:CO₂ mole ratio was initially about 6 but decreased to about unity in the final stages of reaction. With UC and 16 M HNO₃, the NO₂:CO₂ mole ratio decreased from 10 to 20 to about 3. Approximate over-all compositions of the gases evolved in 24-hr. reactions

of the uranium carbides with 4 and 16 M HNO₃ are given in Table II.

Table II. Approximate Compositions of the Gases Evolved in Reactions of the Uranium Carbides with Nitric Acid at 90°^a

Carbide	HNO ₃ concn., M	Gas composition, mole %			
		NO	NO ₂	N ₂ O	CO ₂
UC	4	74	12	2	12
UC ^b	16	7	88	0	5
U ₃ (C ₂) ₃	4	74	8	4	14
U ₃ (C ₂) ₃	16	26	62	1	11
UC ₁₋₈₅	4	68	11	3	18
UC ₁₋₈₅	16	21	65	1	13

^a Reaction time, 24 hr. ^b Reaction time in this experiment was only 6 hr.

Soluble Organic Products. The reactions of the uranium carbides with 4 and 16 M HNO₃ yielded uranyl nitrate and mixtures of soluble, acidic, organic compounds some of which were red-brown in color. Free carbon was not found except when it was originally present in the carbide in concentrations of 0.3% or higher. The organic products were polyfunctional as indicated by their solubility in polar solvents and insolubility in nonpolar solvents like benzene and CCl₄. After separation from the uranyl nitrate and nitric acid, the organic products contained 6 to 40% water. Their equivalent weights, calculated on a water-free basis, were in the range of 60 to 80 g./equiv. and showed no trend with reaction conditions (Table III). The organic products contained between 36 and 46% carbon (Table III). The H:C atom ratios were about 2 (excluding water), while the N:C ratios ranged from 0.02 to 0.07. The organic products did not melt or decompose at 225°; however, oxalic acid sublimed when it was present. Mellitic acid and oxalic acid dihydrate (if present) were detected in the organic products by X-ray diffraction analysis.

Table III. Analyses of Organic Products from the Reactions of Uranium Carbides with Nitric Acid^a

Expt.	Carbide specimen used	Reaction conditions			Analyses ^b	
		Time, hr.	Temp., °C.	HNO ₃ concn., M	C, wt. %	Equiv. wt., g./equiv.
1	AI-4	336	40	4	40	62
2	AI-4	24	105	4	44	66
3	ORNL-1A	24	105	4	42	73
	ORNL-1B					
	ORNL-1E					
4	AI-4	840	25	16	36	61
5	ORNL-1A	24	120	16	44	69
6	U ₂ C ₃ -1A	24	105	4	46	66
7	U ₂ C ₃ -9A	24	120	16	46	83
	U ₂ C ₃ -13A					
8	UC ₂ -16H	24	105	4	41	78
	UC ₂ -18A					


^a Water-free basis. ^b Uranium concentration, <400 p.p.m. in each product.

The infrared spectra of the mixtures were quite similar, irrespective of the carbide or reaction conditions used. The major absorption bands and their assignments are given in Table IV. The spectra were

(12) A. D. Horton and J. L. Botts, *Nucl. Sci. Eng.*, 18, 97 (1964).

(13) J. Katz, S. Abraham, and N. Baker, *Anal. Chem.*, 26, 1503 (1954).

Table IV. Major Absorption Bands in the Infrared Spectra of the Organic Products from the Reactions of Uranium Carbides with Nitric Acid

Frequency, cm. ⁻¹	Intensity ^a	Assignment
720-730	m	 skeletal deformation in oxalic acid
855-870	m	Multisubstituted aromatic
1185-1285	s	-C-O (COOH)
1350	w	-CH ₃
1410	m	-COOH
1380-1460	m	-CH ₂ -, C-CH ₃
1550-1650	m	H ₂ O
1650-1750	vs	-C=O (COOH)
2400-2700	m	-COOH
2920-3000	m	C-H
3100-3300	s	OH, bonded
3360-3520	vs	OH, free

^a m, medium; s, strong; vs, very strong; w, weak.

consistent with those expected from mixtures of oxalic acid and aromatics highly substituted with -COOH and -OH groups, and resembled that of mellitic acid, except for the band at 720-730 cm.⁻¹ which is probably due to the O=C-O skeletal deformation in oxalic acid.¹⁴ This band disappeared after removal of the oxalic acid by vacuum sublimation. Bands due to the aromatic ring, usually present at about 1500 and 1600 cm.⁻¹, were missing from all spectra. These bands were also missing in the spectra of mellitic acid, benzenepentacarboxylic acid, hexa- and pentamethylbenzenes, and hexamethylmellitate, but were observed in the spectra of aromatic compounds which were not as highly substituted; e.g., pyromellitic acid, trimellitic acid, benzoic acid, etc. No bands for the nitro group were observed.

The organic products contained 21 to 44% of the original carbide carbon (Table V). This is consistent with the gas studies¹⁰ in which 50 to 70% of the car-

Table V. Carbon Distribution in the Reactions of Uranium Carbides with Nitric Acid

Expt.	HNO ₃ concn., M	Temp., °C.	—Amount of carbide carbon as organic— products, % of original			
			Total C	Oxalic acid	Mellitic acid ^a	Unidentified
1	4	40	44	8.9	8.9	27
2	4	105	35	2.6	8.4	24
3	4	105	32	1.6	5.9	24
4	16	25	35	10.8	3.8	20
5	16	120	21	0.0	7.9	13
6	4	105	40	5.4	2.6	32
7	16	120	26	0.0	4.0	22
8	4	105	44	4.6	2.4	37

^a Calculated from weight of ammonium salt.

bon was converted to CO₂. The amount of oxalic acid in the products, as determined by vacuum sublimation, varied both with the reaction temperature and the nitric acid concentration (Table V). Reaction with boiling 16 M HNO₃ for 24 hr. left no oxalic acid in solution, whereas boiling 4 M HNO₃ left 2 to 5% of the

(14) D. Hadzi and N. Sheppard, *Proc. Roy. Soc. (London)*, **A216**, 247 (1953).

original carbide carbon as oxalic acid. At 25°, UC yielded products containing 42% oxalic acid (11% of the original carbide carbon; Table V). Mellitic acid, as determined by precipitation of the ammonium salt, accounted for 4 to 9% of the carbon in UC; the yields from the sesqui- and dicarbides were lower, only 2 to 4% of the carbide carbon (Table V).

Since less than half of the carbon in the organic products could be accounted for by oxalic and mellitic acids, attempts were made to further resolve the mixtures by paper and partition chromatography. These experiments showed that the lower benzene and aliphatic acids were not present in significant quantities. Ascending paper chromatography with ethanolic NH₄OH as the solvent¹⁵ resulted only in a spot at R_f = 0.6 to 0.7. This R_f value corresponded to both oxalic and trimellitic acids. After removing the oxalic acid by vacuum sublimation, no spot was found. R_f values for the pure benzene acids varied from 0 for mellitic and benzenepentacarboxylic acids to about 0.9 for benzoic acid. Benzenetetracarboxylic acids gave R_f values of 0.3 to 0.4. Thus, these tests further proved the existence of oxalic acid in the organic products and showed that little or no benzene acids containing fewer than five carboxyl groups were present. Attempts were also made to separate the mixtures by partition chromatography^{11,16} using dilute sulfuric acid on a silica gel support with butanol-chloroform solutions as the eluting solvents. Generally nothing eluted from the column, although, in some cases, small peaks were obtained which could have been pyromellitic acid. This compound could not be isolated and identified. Assuming that this compound was pyromellitic acid, it would account for less than 1% of the carbide carbon. Benzene acids containing 1 to 4 carboxyl groups¹¹ and several aliphatic mono- and dicarboxylic acids¹⁷ elute under these conditions; therefore, components such as these were not among the organic products in significant amounts.

Discussion

Mellitic and oxalic acids, and other soluble organic species, were formed during the reactions of the uranium carbides with nitric acid even when practically no free carbon was present in the carbide. Although the unidentified species could not be isolated, their equivalent weights (estimated at 75 to 85 g./equiv.), solubility behavior, and infrared spectra indicate the presence of complex, aromatic, polyfunctional acids or hydroxy acids. These results are in general agreement with those of prior workers²⁻⁴; however, the organic products obtained by Simpson and Heath² had equivalent weights of 100 to 150 (water content unknown), whereas those obtained in this study were 60 to 80. Our results are also at variance with those of Simpson and Heath, Pausen, *et al.*,⁴ and Pollard, *et al.*,⁶ regarding the amount of carbide carbon converted to CO₂ and the composition of the gases evolved. Simpson and Heath found no carbon-containing compounds in the gases and assumed that all of the carbide carbon was converted to soluble species. Pausen, *et al.*, found only up to 40% of the carbide carbon as CO₂. In our

(15) A. L. Clingman and D. A. Sutton, *Fuel*, **31**, 259 (1952).

(16) B. Fishwick, *J. Chem. Soc.*, 1196 (1957).

(17) C. S. Marvel and R. D. Rands, *J. Am. Chem. Soc.*, **72**, 2642 (1950).

experiments, at least 50% of the carbide carbon was converted to CO₂. Pollard, *et al.*, did not report the presence of CO₂ in the gases evolved from the reaction of UC with 4 M HNO₃, although it could have been present in the 15% of the gas which was not identified. They reported, however, that the gas contained 65% methane. This result contrasts markedly with our finding that no hydrocarbons were produced even in reactions with dilute nitric acid. A more critical comparison of results cannot be made since, in general, details of the experimental conditions, analyses of the carbides used, volumes of the gases evolved, and analyses of both the solid and gaseous reaction products were not reported by other workers.

Pausen, *et al.*,⁴ suggested that graphite was formed as an intermediate in the reactions and served as a precursor to the soluble organic species. This hypothesis was based primarily on the fact that the oxidation products from the carbides were very similar to those obtained from the nitric acid oxidation of graphite. While this hypothesis may be correct, we suspect another mechanism, since, in our study, free carbon was not found (except when it was present in the carbide as free graphite), even when the reaction was conducted at room temperature. Deposition of carbon during reaction, which was reported by other workers,^{3,5} could well have been the result of free carbon in their carbides, since they did not analyze them for free carbon. Furthermore, it is very difficult to envisage the formation of graphite, particularly in the case of UC, where each carbon atom in the crystal lattice is surrounded by six uranium atoms and virtually no C-C bonding exists (the closest C-C distance is 3.5 Å).¹⁸

The possibility of forming aromatic compounds and oxalic acid by polymerization of radicals such as HCO, :CO, and :CH₂, which could be formed from single C units, seems more probable than the formation of a graphite intermediate.

The formation of aromatic compounds in reactions of the uranium carbides with nitric acid is particularly intriguing considering the fact that only aliphatic hydrocarbons are evolved during hydrolysis in water.⁷⁻⁹ These hydrocarbons are essentially those expected considering the structures of the compounds. For example, UC, which contains single C units in the crystal, yields primarily methane, while the sesqui- and dicarbides, which contain C₂ units in the crystal, yield hydrocarbons containing two, or multiples of two, carbon atoms per molecule. It is evident from the foregoing that much more work will be required before the mechanism of the carbide-nitric acid reactions is elucidated.

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(18) A. E. Austin, *Acta Cryst.*, **12**, 159 (1959).