ture of $W_{20}O_{58}$ and $W_{18}O_{49}$ (over-all composition $WO_{2.82}$) is significantly greater than the values reported for each of the nearly pure phases.

The existence of additional defect structures prepared under different conditions and having compositions differing only slightly from that of $WO_{2.96}$ remains a distinct possibility. The recent observations by Gado[6,16] indicate a structure which is quite different from that proposed here, and the observations by Kellett and Rogers[17] may indicate a new phase which is different from those previously observed.

Acknowledgments.—The authors wish to acknowledge Mr. James H. Maurer for assistance in the preparation of samples and Dr. Stanley Siegel for useful criticism and discussion throughout the course of this investigation.

(16) P. Gado, Research Institute for Telecomm. Techn., Budapest, Hungary, private communication.

(17) E. A. Kellett and S. E. Rogers, *J. Electrochem. Soc.*, **110**, 502 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF TEXAS, AUSTIN, TEXAS

The Crystal Structure of Lanthanum Telluride and Tellurium-Deficient Neodymium Telluride[1]

BY R. WANG, H. STEINFINK, AND W. F. BRADLEY

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Single crystal X-ray diffraction studies of $LaTe_2$ and $NdTe_2$ and of the related tellurium-deficient compositions have confirmed the isomorphism with Fe_2As (C 38). Two different types of tellurium atoms exist in the structure. The atoms in the basal plane are essentially metallic in nature and give rise to the observed electrical properties. These are the atoms which can be removed from the structure to produce the tellurium-deficient compositions. This explains the increased electrical resistivity as well as the decrease in the length of the a axis and the increase in the length of the c axis observed for these compounds.

Introduction

The crystal structure of $LaTe_2$ was reported as isostructural with $CeTe_2$ by Pardo, Flahaut, and Domange,[2,3] and both compounds appear to be isostructural with the Fe_2As structure, C 38.[4] Since lanthanum and cerium have atomic numbers which are close to the atomic number of tellurium, the differences in atomic scattering factors, especially after applying a dispersion correction, are small enough to prevent the unequivocal assignment of locations for these atoms. The previous structure investigations were based on data derived from powder patterns. Investigation of the structures of the two isomorphs $NdTe_2$ and $LaTe_2$ by means of single crystal techniques promises to locate definitely the atomic species. The neodymium compound, with the greater scattering factor difference, was also deficient in tellurium. It afforded a firm distribution of the atomic species among alternative equivalent position sets, which could then be applied to the $LaTe_2$.

Experimental Section

Lanthanum and neodymium were treated with tellurium by a vapor–solid reaction in sealed Vycor tubing at 600° to yield compounds having formulas $LaTe_{2.0}$ and $NdTe_{1.8}$. The space group for these compounds is $P{}^4/{}_nmm$, and the unit cell constants obtained from powder data are $a = 4.507 \pm 0.005$ Å., $c = 9.128 \pm 0.010$ Å. for $LaTe_{2.0}$ and $a = 4.377 \pm 0.005$ Å., $c = 9.060 \pm 0.010$ Å. for $NdTe_{1.8}$; there are 2 formula weights per unit cell. The room temperature variation of lattice constants c, a, and c/a as a function of composition for the $NdTe_{2-x}$ solid solution range has been reported by Lin, Steinfink, and Weiss.[5]

Single crystals of $LaTe_{2.0}$ of dimensions $0.07 \times 0.06 \times 0.007$ mm. and of the approximate composition $NdTe_{1.8}$ of dimensions $0.05 \times 0.04 \times 0.01$ mm. were mounted along the c axis. The three-dimensional intensity data from both crystals were collected with a G.E. XRD-5 single crystal orienter using Cu Kα radiation and a scintillation counter with pulse height discrimination. Absorption corrections were necessary because of the high linear absorption coefficients of $LaTe_2$ and $NdTe_2$, 2126.7 and 2370.5 cm.$^{-1}$, respectively. The shapes of the somewhat irregular fragments were approximated by a small number of boundary planes, and the absorption corrections were computed by the Busing and Levy method.[6] This shape approximation of the fragment was rather idealized for the two large dimensions, making the $hk0$ reflections subject to large absorption errors. In this structure the x and y parameters are fixed by symmetry so the $hk0$ reflections were omitted from the refinement calculations.

The scattering factors of La, Nd, and Te were corrected for dispersion, isotropic as well as anisotropic temperature factors were used, and a full-matrix, least-squares refinement with unit weights was carried out based on the Fe_2As model.

Structure Determination

Table I shows the final positional parameters and the anisotropic temperature factors together with their

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(1) Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 806-65.

(2) M. P. Pardo, J. Flahaut, and L. Domange, *Compt. rend.*, **256**, 953 (1963).

(3) M. P. Pardo, J. Flahaut, and L. Domange, *Bull. soc. chim. France*, 3267 (1964).

(4) A. F. Wells, Structural Inorganic Chemistry, 3rd Ed., Oxford University Press, London, 1961, p. 520.

(5) W. Lin, H. Steinfink, and E. J. Weiss, *Inorg. Chem.*, **4**, 877 (1965).

(6) W. R. Busing and H. A. Levy, *Acta Cryst.*, **10**, 180 (1957).

TABLE I

FINAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR $LaTe_{2.0}$

	x	y	z	$B_{11} = B_{22}$	B_{33}
Te(1)	0	0	0	0.02423	0.00028
Te(2)	0	$^1/_2$	0.36686	0.00423	0.00137
La	0	$^1/_2$	0.72395	0.00853	0.00089

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS OBTAINED WITH Cu Kα FOR THE COMPOSITION $LaTe_{2.0}$

H	K	L	FOB	FCAL	H	K	L	FOB	FCAL
0	0	1	9.7	15.6	1	1	9	123.1	120.5
0	0	2	9.7	−11.2	1	1	10	73.7	65.9
0	0	3	210.5	201.7	1	2	1	28.9	−22.6
0	0	4	80.4	71.3	1	2	2	52.2	−47.7
0	0	5	63.4	52.7	1	2	3	116.9	106.9
0	0	6	51.3	48.4	1	2	4	30.9	−29.6
0	0	7	66.9	69.8	1	2	5	114.5	−99.2
0	0	8	136.8	125.3	1	2	6	113.9	107.4
0	0	9	21.3	−17.9	1	2	8	78.7	−72.9
0	0	10	21.8	32.2	1	2	9	36.3	38.8
0	0	11	134.3	136.5	1	3	1	95.4	106.2
1	0	2	64.0	−56.9	1	3	2	115.8	119.7
1	0	3	134.4	126.4	1	3	3	37.9	−28.7
1	0	4	32.8	−34.7	1	3	4	58.3	57.1
1	0	5	127.5	−112.4	1	3	5	58.7	61.1
1	0	6	126.8	120.0	1	3	6	62.7	58.9
1	0	8	80.2	−79.9	1	3	7	41.2	38.9
1	0	9	40.3	41.6	1	3	8	26.3	−14.3
2	0	3	165.2	162.6	1	3	9	95.3	97.3
2	0	4	62.5	55.2	1	4	3	74.2	77.1
2	0	5	52.9	42.3	1	4	5	79.3	−75.1
2	0	6	41.5	39.3	1	4	6	82.3	82.9
2	0	7	55.6	58.2	1	5	3	33.2	−29.7
2	0	8	121.8	111.0	2	2	2	16.9	−15.8
2	0	9	21.3	−19.7	2	2	3	134.9	138.5
3	0	2	45.1	−42.4	2	2	4	48.7	44.1
3	0	3	101.0	94.2	2	2	5	42.4	34.7
3	0	5	99.8	−89.4	2	2	6	31.7	32.4
3	0	6	101.6	97.6	2	2	7	47.7	49.1
3	0	8	68.0	−67.0	2	2	8	108.4	99.2
3	0	9	33.2	36.4	2	2	9	22.4	−21.0
4	0	3	105.4	107.2	2	3	3	80.4	−84.7
4	0	4	37.2	29.1	2	3	5	84.9	81.5
4	0	5	30.5	24.3	2	3	6	91.3	−89.6
4	0	6	23.4	22.6	2	3	8	61.1	62.0
4	0	7	34.6	35.4	2	4	3	83.8	96.1
5	0	3	59.5	65.6	2	4	4	23.4	23.7
5	0	5	63.4	−65.0	3	3	1	69.5	81.4
1	1	1	126.1	156.3	3	3	2	85.6	91.8
1	1	2	162.4	173.0	3	3	3	27.2	−29.6
1	1	3	30.9	−27.1	3	3	4	42.1	43.6
1	1	4	86.3	80.4	3	3	5	45.6	45.3
1	1	5	91.4	86.5	3	3	6	47.4	44.5
1	1	6	92.5	81.2	3	3	7	30.9	29.9
1	1	7	63.8	52.7	3	4	3	56.6	65.6
1	1	8	6.9	−9.0	3	4	5	60.7	−65.0

standard deviations for $LaTe_{2.0}$. The discrepancy coefficient R is 0.078 for this structural arrangement, labeled A, and the F_o and F_c are listed in Table II. Arrangement A is analogous with that established later for the neodymium compound.

The scattering factors for La and Te are so similar that the effect the interchange of atomic positions would have on the structure factors was tested. Table III summarizes the change in the discrepancy coefficients as a result of the three possible arrangements and the significances of these variations were examined by Hamilton's R factor test.[7] In the isotropic refinement, there are 6 parameters and 92 reflections, so that the dimension of the hypothesis is 6 and the number of degrees of freedom is 86. We find that $R_B/R_A = 1.017$, and structure B cannot be rejected at the 50% confidence level; $R_C/R_A = 1.149$, and, since $\mathcal{R}_{6,86,0.005} = 1.085$, structure C can be safely rejected.

In the anisotropic refinement there are nine parameters, and the number of degrees of freedom is 83. $R_A/R_B = 1.031$, $\mathcal{R}_{9,83,0.50} = 1.049$, and structure B cannot be eliminated. $R_C/R_A = 1.366$ and $\mathcal{R}_{9,83,0.005} = 1.147$ so that structure C can be rejected. The diffraction data would not have afforded a choice between A and B in the $LaTe_2$ composition.

TABLE III

A COMPARISON OF R FOR DIFFERENT ARRANGEMENTS OF La AND Te IN $LaTe_{2.0}$

Structure	0, 0, 0	0, $^1/_2$, 0.367	0, $^1/_2$, 0.724	$R_{\text{isotropic}}$	$R_{\text{anisotropic}}$
A	Te(1)	Te(2)	La	0.121	0.0776
B	Te(1)	La	Te(2)	0.123	0.0753
C	La	Te(2)	Te(1)	0.139	0.1060

TABLE IV

A COMPARISON OF R FOR DIFFERENT ARRANGEMENTS OF Nd AND Te IN A $NdTe_{1.8}$ CRYSTAL CALCULATED AS $NdTe_{2.0}$

Structure	0, 0, 0	0, $^1/_2$, 0.368	0, $^1/_2$, 0.727	$R_{\text{isotropic}}$	$R_{\text{anisotropic}}$
A	Te(1)	Te(2)	Nd	0.118	0.0536
B	Te(1)	Nd	Te(2)	0.135	0.0730
C	Nd	Te(2)	Te(1)	0.136	0.0763

The larger difference in scattering factors between Nd and Te was sufficient to permit an unequivocal assignment of atomic locations. An initial refinement of the $NdTe_{1.8}$ data was made on the assumption that all sites were occupied. Table IV shows the values of R obtained for various models. The application of Hamilton's R test showed that structures B and C could be rejected at the 0.005 significance level for both the isotropic and anisotropic refinements and that structure A was correct.

Once the atomic locations had been determined, the occupancy of the Te(1) site, designated $W_{Te(1)}$, was gradually decreased from 1.0 to 0.75 in the anisotropic least-squares calculation. A minimum R of 0.0448 was obtained for the composition $NdTe_{1.89}$. Again, Hamilton's R test was used to find the significant range for the variation of the stoichiometry.

The number of reflections is 89, and the number of parameters is 9. The dimension of the hypothesis is 1, and the smallest R factor is 0.0448 for the composition $NdTe_{1.89}$. Compositions which can be rejected at the 0.01 significance level must have R factors such that

$$\mathcal{R}_{1,80,0.01} = 1.043 = \frac{R_W}{0.0448}$$

and R_W is thus 0.0468. Figure 1 shows that for this value of R_W the tellurium concentration can range from 0.83 to 0.94.

The final anisotropic parameters of the $NdTe_{1.8}$ crystal calculated as $NdTe_{1.89}$ are listed in Table V, and F_o and F_c for this calculation are shown in Table VI.

The assumption that Te(2) atoms were the ones which are missing in the unit cell increased R to 0.0665 at $W_{Te(1)} = 0.89$. We found this assumption is incorrect after applying Hamilton's R Test. Thus the deficiency of Te atoms occurs only in the basal plane.

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(7) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

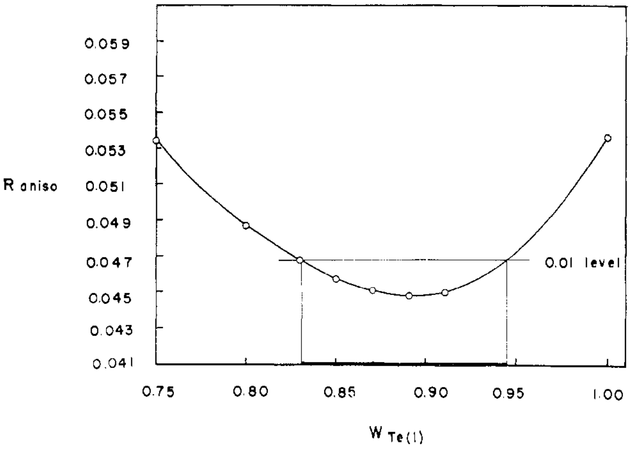

Figure 1.—The 99% confidence interval for $W_{\mathrm{Te(1)}}$ based on a test of $\mathcal{R}$ for $NdTe_{1.8}$ crystal.

Table V

Final Parameters and Standard Deviations for $NdTe_{1.89}$

	x	y	z	$B_{11} = B_{22}$	B_{33}
Te(1)	0	0	0	0.0546_3	0.0019_5
Te(2)	0	$^1/_2$	0.3678_3	0.01742_2	0.0022_5
Nd	0	$^1/_2$	0.7291_3	0.01492_2	0.0037_5

Table VI

Observed and Calculated Structure Factors Obtained with Cu Kα Radiation for a Composition Corresponding to $NdTe_{1.89}$

H	K	L	FOB	FCAL	H	K	L	FOB	FCAL
0	0	3	172.7	180.9	1	4	2	29.7	-29.0
0	0	4	67.3	66.2	1	5	2	54.3	49.7
0	0	5	55.5	54.6	2	2	2	37.7	-30.6
0	0	6	27.4	26.9	3	3	2	57.9	67.5
0	0	7	50.2	48.2	1	1	3	35.5	-29.4
0	0	8	118.2	122.1	1	2	3	101.5	105.2
0	0	9	16.8	-17.6	1	3	3	36.5	-32.0
0	0	10	9.5	9.8	1	4	3	69.3	67.8
0	0	11	98.4	106.1	1	5	3	24.6	-27.9
1	0	1	33.6	-32.8	2	2	3	106.4	106.7
1	0	2	62.6	-61.0	2	3	3	77.0	-77.2
1	0	3	131.4	129.7	2	4	3	66.1	61.3
1	0	4	28.1	26.9	3	3	3	34.8	-30.7
1	0	5	114.1	114.3	3	4	3	53.9	53.6
1	0	6	106.2	104.9	1	1	4	61.4	60.6
1	0	8	57.7	-62.0	1	2	4	24.8	-22.6
1	0	9	25.0	24.9	1	3	4	35.3	31.3
2	0	2	28.4	-28.6	2	2	4	36.7	34.4
2	0	3	138.5	134.6	2	4	4	16.7	15.5
2	0	4	48.2	46.8	1	1	5	61.2	61.6
2	0	5	39.3	37.7	1	2	5	95.9	-96.6
2	0	6	15.4	15.6	1	3	5	33.7	35.5
2	0	7	38.2	35.8	1	4	5	68.2	-64.5
2	0	8	100.6	100.9	2	2	5	28.2	26.5
2	0	9	20.7	-21.1	2	3	5	75.6	73.0
3	0	2	33.5	-39.5	3	3	5	19.8	22.2
3	0	3	89.6	89.2	1	1	6	77.5	77.3
3	0	4	17.3	-19.5	1	2	6	91.3	89.9
3	0	5	78.5	-83.4	1	3	6	50.6	49.0
3	0	6	80.8	78.3	1	4	6	62.6	61.2
3	0	8	51.3	-48.5	2	3	6	71.6	-68.9
3	0	9	20.9	19.1	3	3	6	34.1	33.2
4	0	3	73.1	72.5	1	1	7	48.7	48.1
4	0	4	18.7	19.9	1	3	7	30.0	26.9
4	0	6		-.6	2	2	7	27.6	26.9
4	0	7	19.6	15.8	1	2	8	55.6	-54.6
5	0	3	48.7	53.6	1	3	8	31.8	-31.1
1	1	1	132.0	137.8	2	2	8	83.8	84.6
1	2	1	24.9	-26.3	2	3	8	42.0	43.3
1	3	1	73.6	79.5	1	1	9	91.4	93.8
1	5	1	44.9	37.3	1	2	9	20.7	21.7
3	3	1	45.5	52.8	1	3	9	67.2	66.7
1	1	2	150.2	159.4	2	2	9	24.0	-23.0
1	2	2	47.7	-47.6	1	1	10	57.2	60.7
1	3	2	86.6	97.5					

Table VII

Interatomic Distances in $LaTe_{2.0}$, Å.

Te(1)–Te(1)	3.187
Te(1)–Te(2)	4.036 ± 0.005
Te(2)–Te(2)	4.009 ± 0.008
La–Te(1)	3.381 ± 0.005
La–Te(2)	3.293 ± 0.007
La–Te(2)	3.260 ± 0.007
La–La	5.183 ± 0.006

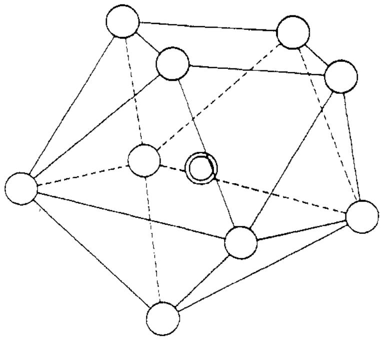

Figure 2.—The tellurium polyhedron around lanthanum.

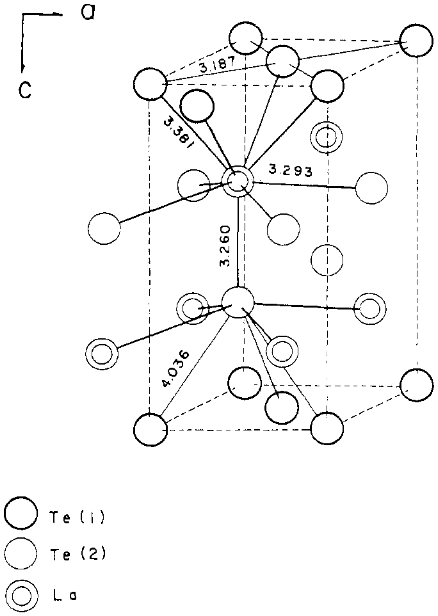

Figure 3.—The atomic configuration in the unit cell of $LaTe_{2.0}$.

Discussion

The interatomic distances observed in $LaTe_2$ are shown in Table VII. The tellurium contacts in the basal plane are considerably shorter than the other Te–Te distances and indicate that these have considerable metallic–covalent character. If the ionic radius for Te^{-2} is taken as 2.2 Å. and the metallic radius is taken as 1.4 Å., then the bonding can be considered as about 72% metallic–covalent. It is indeed observed that the variations of electrical conductivity and of the Seebeck coefficient show that $LaTe_{2.0}$ has the most metallic character of the solid solution series.[8] The shrinkage of the a axis and the elongation of c as the tellurium concentration decreases are also consistent with the removal of atoms from the basal plane.

Lanthanum is located 0.83 Å. above the center of a

(8) T. Ramsey, H. Steinfink, and E. J. Weiss, *J. Appl. Phys.*, **36**, 548 (1965).

square formed by four Te(2) atoms and forms four bonds 3.293 Å. long to these atoms; directly beneath the La atoms is a Te(2) at 3.260 Å. which completes a square pyramid with the other four Te(2); four Te(1) atoms at 3.381 Å. from La form a square 2.52 Å. above La, and this square is rotated 45° with respect to the square pyramid formed by the Te(2) atoms, Figure 2. The shorter La–Te(2) bonds can be ascribed to the more ionic nature of this bond, and the lengthening of La–Te(1) is due to the quite different character of the metalloid in the basal plane of the unit cell. Figure 3 shows the atomic configuration in this structure.

The environment of Te(2) consists of a nearly regular pyramid formed by four La atoms in the base and one La atom at the apex. The 4.036-Å. distance between Te(1) and Te(2) indicates that very little bonding exists between these tellurium layers. The higher temperature factor observed for Te(1) agrees also with the concept that these atoms are different from the tellurium found in sites 2(e) of the space group.

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The Photolysis of Carbon Suboxide

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At room temperature C_3O_2 absorbs light in the region 2492–2700 Å. to give CO and a photopolymer which is the same as the thermal polymer except that ketenyl groups are present. Photopolymerization is shown to be a combination of photonucleation and thermal polymerization on the nuclei; the polymer precipitates from the gas phase and also forms on the cell windows. The presence of O_2 during photolysis eliminates the ketenyl band from the photopolymer spectrum, reduces both the amount of polymer and CO that are formed, and increases the ratio of C_3O_2 used to CO produced. No CO_2 is formed either with or without the presence of O_2. The proposed reaction mechanism features an electronically excited C_3O_2 molecule which may dissociate to give a C_2O radical and CO or be deactivated by a suitable third body (O_2 or C_3O_2), a typical carbene attack by the C_2O radical on C_3O_2 to give C_4O_2, and a nucleation reaction of C_4O_2 with C_3O_2.

Introduction

Recent papers[1,2] have discussed the photolysis of C_3O_2 in the presence of a large excess of ethylene, under which conditions the principal products are allene and CO. Also, it was reported[3] that the photopolymer which is produced by irradiation of C_3O_2 with ultraviolet light is different from the thermal polymer. This paper reports on the photolysis of C_3O_2 without admixture of other gases and in the presence of O_2.

Experimental Section

C_3O_2 was prepared as described earlier.[3] Photolyses were carried out in evacuable Pyrex cells which were 14 mm. long and 25 mm. in diameter, with 3-mm. thick BaF_2 windows sealed at each end with Kronig cement. The 13-cm. lead of 4-mm. tubing between the cell and the stopcock was bent so that the bend could be immersed in liquid N_2 and so that the cell and stopcock could be placed in the cell compartment of a Cary Model 14 spectrophotometer. The filtered radiation from a Hanovia 673A mercury vapor lamp was used for photolysis. The filter was composed of two solutions contained in silica cells: (a) 46 g. of $NiSO_4 \cdot 6H_2O$ and 14 g. of $CoSO_4 \cdot 7H_2O$ in 100 ml. of H_2O, and (b) 0.108 g. of I_2 and 0.155 g. of KI in 1 l. of H_2O. The energy distribution calculated to be incident on the photolysis cell was determined using the lamp manufacturer's rated energy output at each wave length and an experimentally determined absorption curve for the filter. The percentage distribution at the most intense wave lengths in this region was 1.6% at 3341, 27.7% at 3130, 4.8% at 3025, 1.2% at 2967, 1.6% at 2700, 16.9% at 2652, 11.3% at 2571, 29.9% at 2537, and 3.5% at 2482 Å. By combining these values with the molar extinction coefficients of C_3O_2 it was calculated that 90% of the absorbed radiation lay between 2652 and 2537 Å., or 96.5% between 2700 and 2482 Å. In the few measurements made at 3130 Å. a filter was used in which solution (b) above was replaced by one containing 0.5 g. of potassium hydrogen phthalate per 100 ml. Calculations and experiments similar to those just described showed that 88% of the photolytic radiation transmitted by this filter was at 3130 Å. and 12% was at 3341 Å. One of the main products of irradiation is a tan photopolymer which deposits in part on the windows and soon prevents the further absorption of more light; photolysis ceases. The spectrum of this photopolymer was determined with Cary Model 14 and Perkin-Elmer Model 21 spectrophotometers after first removing all gases for analysis. In an effort to minimize the volume and to exclude Hg vapor (and the possibility of Hg photosensitization) all gas pressures were measured with an all-glass spiral gauge which, together with the optical lever, had an over-all sensitivity of ±0.08 mm.

In analyzing for CO, the bend in the stem of the photolysis cell was immersed in liquid N_2 to freeze out any C_3O_2 and CO_2. When CO was the only noncondensable gas, it was allowed to expand from the cell to a small volume which included the spiral gauge; calibration measurements related the observed pressure to the CO pressure which had existed in the cell before expansion. When CO was mixed with O_2, the two gases were drawn through a 4-mm. tube tightly packed with Pt gauze and heated electrically to 500°; the CO thus converted to CO_2 was frozen out in a small U tube while the remaining O_2 was completely removed from the system by pumping. The CO_2 (formerly CO) was transferred with the aid of liquid N_2 to a small finger trap attached to the small-volume system, its pressure was measured at room tem-

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[1] (a) K. D. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961); (b) *ibid.*, **84**, 4077 (1962); (c) *ibid.*, **85**, 1730 (1963); (d) *Bull. soc. chim. Belges*, **71**, 724 (1962).

[2] R. T. Mullen and A. P. Wolf, *J. Am. Chem. Soc.*, **84**, 3214 (1962).

[3] R. N. Smith, D. A. Young, E. N. Smith, and C. C. Carter, *Inorg. Chem.*, **2**, 829 (1963).