Discussion

With the exception of $Ba(Sr_{1/3}Ta_{2/3})O_3$, the powder patterns of the compounds listed in Table I contained the lines of a cubic cell of the size indicated. These compounds may be considered as having undistorted pseudocells of cubic shape with an edge of about 4 Å. "Extra" lines were noted, however, in all cases except those designated by a superscript *a*. Almost all of the extra lines of the $Sr^{II}(B_{1/3}{}^{II}Ta_{2/3}{}^{V})O_3$ compounds could be accounted for by a cubic cell of three times the indicated pseudocell edge.

For $Ba(Sr_{1/3}Ta_{2/3})O_3$ that pseudocell was clearly distorted and the size reported was based on the first few lines of the photograph. The lattice may be rhombohedral with a unit cell edge about three times the indicated pseudocell edge and the rhombohedral angle close to 90°.

In Table III some series of solid solutions and some oxygen deficient phases are listed. Those compounds for which no "extra" lines were observed are designated by an *a*. Compounds which have cubic cells of twice the indicated pseudocell length, as previously discussed, are designated by *b*.

Some of the compounds listed in Table III may be considered solid solutions of other compounds listed in Tables I and III. For example, $Ba(Zn_{1/5}Fe_{1/5}{}^{III}Ta_{3/5})O_3$ may be considered a solid solution of $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Fe_{1/2}Ta_{1/2})O_3$. Although it is possible that single phases exist over the complete ranges of solid solution, the only intermediate phases prepared in this study are those listed in the table.

Two factors which help determine whether an arrangement of different ions in B positions of a perovskite type structure will be ordered or random are ionic sizes and charge difference. The $A(B_{1/2}{}^{II}W_{1/2}{}^{VI})O_3$ compounds, where A is Ba or Sr, have an ordered arrangement for a variety of B cations of different sizes.[4] Ordering can reduce local violations of Pauling's electrostatic valence rule and may therefore be expected in such an extreme case of ionic charge difference. Where the charge difference is not so great, as in the cases of $Ba(La_{1/2}Ta_{1/2})O_3$,[6] which has an ordered arrangement of La and Ta, and $Ba(Fe_{1/2}{}^{III}Ta_{1/2})O_3$, which, as prepared in this study, appears to have a random arrangement of Fe and Ta, size could be the determining factor. The size of the La^{III} ion (ionic radius = 1.15 Å.) would cause an ordered arrangement to be favored if the perovskite type structure is to be maintained, whereas the Fe^{III} ion (0.67 Å.) is small enough to be accommodated in a random arrangement. Such compounds as $Ba(Ba_{1/2}Nb_{1/2})O_{2.75}$ and $Sr(Sr_{1/2}Nb_{1/2})O_{2.75}$ have large ions in the B positions and the ordering observed is therefore to be expected. The ordering together with the oxygen deficiency may be the primary factors in the retention of cubic cell shape in these compounds.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS AND THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Molecular Complexes and Their Spectra. IX. Infrared Absorption by Iodine in its Pyridine Complexes and in Benzene

BY EARLE K. PLYLER AND ROBERT S. MULLIKEN

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When iodine and pyridine (Py) are dissolved together, the iodine fundamental vibration is absorbed rather strongly with a frequency ω_0 shifted from its vapor value (213 cm.$^{-1}$) to 184 cm.$^{-1}$ (in *n*-heptane) or 174 cm.$^{-1}$ (in benzene). In Bz (benzene), very much weaker absorption at 204 cm.$^{-1}$ is also observed. Quantitative intensity curves are shown. The shifted absorptions are ascribed, respectively, to a $Py\cdot I_2$ or a $Bz\cdot I_2$ charge-transfer complex (or perhaps contact, in the Bz case). Further details of interpretation and comparisons with other pyridine and benzene complexes of the halogens are given. Preliminary experiments showed that it is necessary to work with fairly fresh solutions, otherwise a band of unknown origin appears at 214 cm.$^{-1}$. Iodine in *n*-heptane (0.02 *M*) produces no new peaks near 200 cm.$^{-1}$.

Introduction

According to the quantum-mechanical theory of 1:1 donor–acceptor complexes with a halogen molecule X_2 or XY as acceptor, the X–X or X–Y bond should be loosened, the more so the greater the amount of negative charge transferred from the donor to the halogen molecule.[1] This loosening should be manifested by an increase in interatomic distance and a decrease in vibration frequency for the halogen. The former effect is best studied in solid compounds, and Hassel and collaborators have demonstrated its occurrence in a number of complexes with donors of the pyridine and the ether classes.[2] The latter effect is most easily studied by seeking the halogen molecule fundamental in the infrared absorption spectra of 1:1 complexes in solution.

Recently, D'Or, Collin and collaborators[3] have shown that (although the free halogen molecules Cl_2, Br_2 and I_2 are of course infrared-inactive) the infrared fundamental of Cl_2 and Br_2 appears, weakly and appreciably shifted toward lower frequency, in the absorption spectra of their solutions in benzene. This is what is expected if the halogen molecules are in part bound in charge-transfer complexes. However, for the halogens in benzene, perhaps the interactions should be described in terms of "contacts" rather than of complex-formation.[4] Still, it seems clear that they are in any

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(1) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952), II of the present series.

(2) O. Hassel, *Proc. Chem. Soc.*, 250 (1957); *J. Mol. Spec.*, 1958.

(3) J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955); L. D'Or, R. Alewaeters and J. Collin, *Rec. trav. chim.*, **75**, 862 (1956).

(4) L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957), VII of this series.

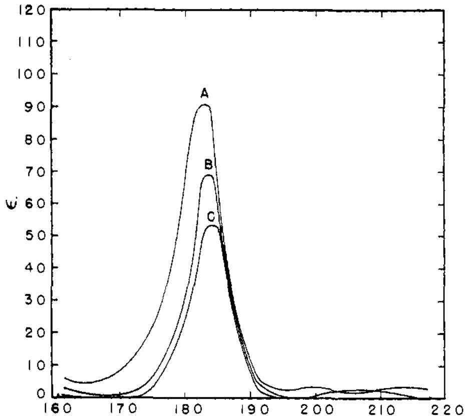

Fig. 1.—Plot of extinction coefficient [$\epsilon = 1/lc \log (I_0/I)$, where l = cell thickness, and c = formal molarity based on total iodine] against wave number (cm.$^{-1}$) for 0.1 M iodine solutions in n-heptane, with decreasing amounts of pyridine. Room temperature, cell thickness 0.4 cm.; A, pyridine 0.3 M; B, pyridine 0.05 M; C, pyridine 0.0125 M.

event donor–acceptor interactions involving partial charge transfer, differing only in degree and not in kind from those which lead to definite strongly bound halogen complexes such as those with pyridine or triethylamine as donor.[5]

A question of interest here is the orientation of the halogen molecule in its contacts or complexes with benzene. Mulliken, thinking in terms of definite complexes, argued that the orientation must be one of low symmetry in order to account for the activation of the infrared halogen frequency.[6a] Ferguson and Matsen, however, show that activation could also occur even for high symmetry.[6b] But for the case of benzene as donor, predominance of random orientations seems likely in view of the weakness of the interactions.[4] In strong complexes, however, definite orientations are expected, and these have been established in the case of solid halogen complexes.[2]

The results of d'Or and Collin on the infrared spectrum of Br_2 in benzene were confirmed[7a] by Person and collaborators, and extended to include the interactions of ICl with benzene and other donors.[7b] Of course ICl alone is already infrared-active, but the intensity of its fundamental is increased and its frequency decreased by interaction with benzene and much more strongly with stronger donors.

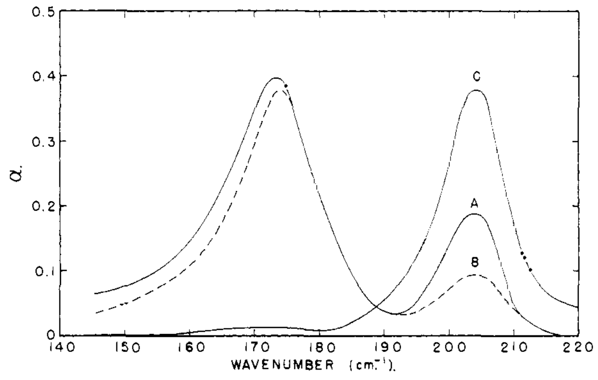

Fig. 2.—Plot of absorption coefficient [$\alpha = \log (I_0/I)$] against wave number (cm.$^{-1}$) for 0.01 M pyridine in benzene, with decreasing amounts of iodine. Room temperature, cell thickness 0.4 cm.; A, iodine 0.3 M; B, iodine 0.1 M. C, iodine 0.4 M with no pyridine present.

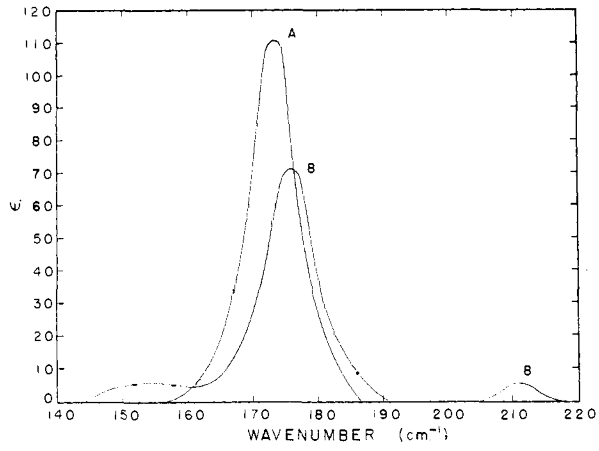

Fig. 3.—Plot of extinction coefficient (based on total iodine as in Fig. 1) against wave number (cm.$^{-1}$) for 0.01 M iodine solutions in benzene, with decreasing amounts of pyridine. Room temperature, cell thickness 0.4 cm.; A, pyridine 0.5 M; B, pyridine 0.1 M.

Since the spectra of iodine complexes have been a subject of particularly intensive study ever since their characteristic ultraviolet bands were discovered by Benesi and Hildebrand,[8] it seemed of especial interest to look for the infrared iodine fundamental activated by charge-transfer interaction. Such a search has hitherto been inhibited by the inaccessibility of the spectral region (ω_0 for I_2 vapor is 213 cm.$^{-1}$) for most instruments. Having the necessary equipment at the Bureau of Standards, we have now established the presence of weak I_2 absorption in benzene at 205 cm.$^{-1}$, and of much stronger absorption near 180 cm.$^{-1}$ in I_2 solutions containing pyridine (Figs. 1–3). We hope to repeat these studies with greater accuracy, and extend them, using a vacuum spectrograph now under construction.

Experimental

The absorption spectrum was measured in the region from 160 to 220 cm.$^{-1}$ with a small grating spectrometer.[9] The instrument was not enclosed *in vacuo* and the rotational lines of water vapor were of considerable intensity in the region. The transmission of solutions was determined by comparing the energy at the maxima between the water lines. The absorption cell was 4 mm. thick and had quartz windows of 0.5 mm. thickness. When the cell was filled with benzene, about 20% of the radiant energy was transmitted, and the benzene–iodine mixtures transmitted from 5 to 20% of the energy. On account of the low transmission of the cell and the irregular background produced by the vapor, the transmission could not be determined to a high precision. It is estimated that the transmission measurements are accurate to ±4%.

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[5] (a) C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954), IV of this series; (b) S. Nagakura, *ibid.*, **80**, 520 (1958), VIII of this series; (c) A. I. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957).

[6] (a) R. S. Mulliken, *J. Chem. Phys.*, **23**, 297 (1955), V of this series. (b) E. E. Ferguson and F. A. Matsen, *ibid.*, **29**, 105 (1958).

[7] (a) W. B. Person, R. E. Erickson and R. E. Buckles, *ibid.*, **27**, 1111 (1957). (b) W. B. Person, R. E. Humphrey, W. A. Deskin and A. I. Popov, THIS JOURNAL, **80**, 2049 (1958).

[8] H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949).

[9] E. K. Plyler and N. Acquista, *J. Chem. Phys.*, **23**, 752 (1955).

TABLE I

EXTINCTION COEFFICIENTS FOR IODINE INFRARED FUNDAMENTAL DUE TO COMPLEXING WITH PYRIDINE

Solvent	Curve	Concn. (mole/l.)			Frequencies (cm.$^{-1}$)		Peak molar extinction coefficients (ϵ_{max})	
		Total Py	Total I_2	Calcd. $Py.I_2$[a]	Peak	Half-intensity width	Based on total I_2	Based on calcd. PyI_2
n-Heptane	A	0.3	0.01	0.0098	183	8	91	93
(Fig. 1)	B	.05	.01	.0089	184	6	68	76
	C	.0125	.01	.0058	184	7	53	91
Benzene	A	.01	.30	.0098	173	17		101
(Fig. 2)	B	.01	.10	.0095	174	16		99
Benzene	A	.5	.01	.0099	174	8	112	113
(Fig. 3)	B	.1	.01	.0095	176	8	72	76

[a] Assuming $K_c = 200$ for $(Py\cdot I_2)/(Py)(I_2)$ in all cases.

The iodine was of reagent grade and the n-heptane, pyridine and benzene were obtained from Eastman, the latter being spectro grade. No further purification of the compounds was made.

The observed transmittance varied slightly for different runs of solutions of the same concentrations. In some cases background absorption would be observed throughout the spectral region (140–220 cm.$^{-1}$). This difference in transmission may in part be caused by small amounts of water in the solution. When small quantities of water were added to fresh solutions a general absorption appeared throughout the spectral region. Some solutions were prepared after the compounds had been dried, but there was no change in the position of the characteristic bands which were observed in undried solutions.

Solutions which had been prepared several days in advance of measurement showed a difference in the spectrum from fresh solutions. In the old solutions of iodine in benzene a strong absorption band of unknown origin appeared at 214 cm.$^{-1}$ (the close agreement with ω_0 of iodine vapor is probably a coincidence), while for fresh solutions the absorption was very small in this region and the maximum of absorption was at 204 cm.$^{-1}$. All the solutions whose spectra are shown in Figs. 1, 2 and 3 were measured the same day they were prepared.

It was thought that the strong absorption of iodine in benzene at 204 cm.$^{-1}$ might possibly be produced by the iodine bringing out inactive vibrations in the benzene.[10] If this were the origin of the absorption, then a bromine-benzene mixture should also give rise to bands in this region. A bromine–benzene mixture containing 0.4 M bromine was measured in the region from 180 to 220 cm.$^{-1}$ and no absorption was observed. From this experiment it was concluded that the absorption at 204 cm.$^{-1}$ did not arise in the benzene molecule but in the iodine molecule in the presence of benzene.

Some runs on 0.02 M iodine (the limit of solubility) in n-heptane showed no absorption near 200 cm.$^{-1}$ due to the iodine.

Discussion

Figure 1 shows our findings for 0.01 M iodine in n-heptane solution with varying amounts of added pyridine. The visible and ultraviolet absorption spectra of this same system were studied by Reid and Mulliken, who determined the equilibrium constant for formation of the 1:1 complex $Py\cdot I_2$ at three temperatures. Our infrared data show a strong peak attributable to complexed I_2 at 184 cm.$^{-1}$. By interpolation from the results of Reid and Mulliken, the equilibrium constant K_c of $Py + I_2 \rightleftarrows Py\cdot I_2$ is 200 at 26° (our room temperature). For the three Py concentrations of Fig. 1 this yields the calculated $Py\cdot I_2$ concentrations shown in Table I. Assuming negligible absorption by free I_2 and by Py at 184 cm.$^{-1}$, the observed peak extinction coefficients of Fig. 1 (based on total I_2) should be proportional to the calculated concentrations of PyI_2. Within the uncertainty of our measurements, this is true (see Table I).

Let us turn now to Fig. 2C, which shows the absorption spectrum of a 4 mm. layer of 0.4 M I_2 in pure benzene. There is a definite peak at 204 cm.$^{-1}$, which may be attributed to charge-transfer interaction or to formation of a $Bz\cdot I_2$ (benzene–iodine) complex. Table II presents a comparison with similar results obtained from other halogens in benzene solution. The frequency shifts relative to the free-molecule frequency, $\Delta\omega_0/\omega_0$, are similar in all, and indicate a similar extent of loosening of the bond in the halogen molecule by charge-transfer; but distinctly greatest for ICl, where also the equilibrium constant and the visible and ultraviolet spectra indicate stronger charge-transfer interaction than for the homopolar halogens. A word of caution should, however, be added. Namely (1) some decrease in frequency may occur even in inert solvents, depending on the dielectric constant (*e.g.*, to 375 cm.$^{-1}$ for ICl in CCl_4)[7b]; (2) the observed frequency decrease should be ascribed only partly to loosening of the intrahalogen bond, and partly to an increase in effective mass due to partial formation of a donor–halogen bond; still, the second of these effects is a manifestation of intermolecular, we believe essentially charge-transfer, interaction.

TABLE II

HALOGEN MOLECULE INFRARED FUNDAMENTAL FREQUENCIES

Halogen	Frequency data (cm.$^{-1}$)			
		Benzene soln.		
	ω_0 in vapor	ω_0	$\Delta\omega_0/\omega_0$	Half-int. width
Cl_2[a]	557	526	−0.056	
Br_2[a,b]	321	305	− .050	22
I_2[d]	213	204	− .038	12
ICl[c]	381	355	− .068	15

[a] Ref. 3. [b] Ref. 7a. [c] Ref. 7b. [d] Present paper, Fig. 2.

When a small amount of pyridine (0.01 M) is added to a fairly concentrated solution of iodine in benzene, the 204 cm.$^{-1}$ $Bz\cdot I_2$ peak remains with an intensity approximately proportional to the iodine concentration, but a strong new peak also appears at about 174 cm.$^{-1}$ (Fig. 2A, B). There can scarcely be any doubt that this latter peak belongs to the $Py\cdot I_2$ complex; but it is shifted by 10 cm.$^{-1}$ toward lower frequency as compared with its 184 cm.$^{-1}$ position in n-heptane solution, and its half-intensity width is doubled (see Table I). These changes suggest that the $Py\cdot I_2$ may have

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[10] That this happens (weakly) for a few of the benzene vibrations at higher frequencies has been shown by E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956); **26**, 1269, 1357 (1957).

formed a double complex $Bz\cdot Py\cdot I_2$ of donor–acceptor character (thus, for example, the $Py\cdot I_2$ complex, with charge distribution $Py^{+}I_2^{-}$, might perhaps act at its Py end as an acceptor toward Bz as a donor, or at its I_2 end as a donor toward Bz as an acceptor); or perhaps the shift may be due to a "contact" donor–acceptor interaction with the Bz molecules which surround it.

If we nevertheless treat the peaks as due to PyI_2 and assume that the equilibrium constant K_c is the same (200) in benzene as in *n*-heptane, and neglect any loss of activity of the I_2 due to its interaction with the benzene (allowance for this would probably not make a great difference), we compute that 97% of the Py should be complexed for curve A and 87% for curve B. This gives peak molar extinction coefficients for PyI_2 in benzene solution which agree well with those obtained in *n*-heptane (see Table I, last column). However, in view of the doubled peak widths, the total intensities are about double those in heptane.

Returning to a consideration of the 204 cm.$^{-1}$ $Bz\cdot I_2$ peak in Fig. 2, and noting in the case of curves A and B that about 0.01 mole/*l.* of I_2 is used up in forming $Py.I_2$ with the 0.01 mole/*l.* of Py present, the available concentrations of I_2 free to interact with Bz are 0.29 *M*, 0.091 *M* and 0.40 *M* for curves A, B, and C, respectively. Based on the heights of the (absorption coefficient) peaks in Fig. 2, the peak extinction coefficients ϵ_{max} at 204 cm.$^{-1}$ in terms of total available I_2 are then 1.59, 2.41, 2.40 for curves A, B and C, respectively. If one now supposes (but *cf.* ref. 4) that there exists in I_2 solutions in Bz an equilibrium $Bz + I_2 \rightleftarrows Bz\cdot I_2$ with a definite $Bz\cdot I_2$ complex, then for this complex, according to Cromwell and Scott, $K_x = 2.3$.[11] With this value of K_x, one finds for ϵ_{max} for the $Bz\cdot I_2$ *complex* the values 2.26, 2.57, 3.47 from curves A, B and C, respectively, or an average of 2.77.

Turning now to Fig. 3, we see the characteristic peak of the $Py\cdot I_2$ complex or $BzPyI_2$ double complex, again in a solution which is mainly benzene, but this time with a small iodine concentration (0.01 *M*) and large Py concentrations, instead of *vice versa*. As expected, the $Bz\cdot I_2$ peak is missing (the small peak at 212 cm.$^{-1}$ in curve B may be ignored); it should be too weak to detect at 0.01 *M* I_2 concentration. Assuming again that the equilibrium constant K_c for PyI_2 is the same in benzene as in heptane, we compute that 97% of the I_2 should be complexed in the case of the 0.5 *M* and 87% in that of the 0.1 *M* Py solution. The computed ϵ_{max} values based on PyI_2 are now found in good agreement with those from Figs. 1 and 2 (*cf.* Table I). Notably, the *half-intensity widths* are now about the same as in heptane solutions, which indicates that the excess iodine, rather than the benzene, is responsible for the increased widths in the curves of Fig. 2 discussed above.

[11] T. M. Cromwell and R. L. Scott, This Journal, **72**, 3825 (1950). $K_x = (Bz\cdot I_2)/(I_2)[Bz]$, where [Bz] is the mole fraction of Bz (very nearly 1 here).

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Dimorphic Modifications of Dibasic Strontium Phosphate, $SrHPO_4$

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A study of the strontium phosphates has disclosed the existence of two crystalline modifications of dibasic strontium phosphate. These modifications behave similarly in the presence of water; but on firing to convert to the pyrophosphates, they follow separate reaction paths dependent upon the original crystal structure. Analogies to the crystal structures of other phosphates are given.

Introduction

References to detailed studies of the calcium phosphates are easily found,[1-3] and many of these papers contain information on the chemistry of dibasic calcium phosphate, $CaHPO_4$ and its hydrate $CaHPO_4\cdot 2H_2O$. In contrast, with the exception of a phase rule study of the system $SrO–P_2O_5–H_2O$ at 25° by Tartar and Lorah,[4] there has been little work on the chemistry of dibasic strontium phosphate.

Knowledge of the crystal structures of the dibasic phosphates of calcium and strontium is in a similar state. Thus, single-crystal diffraction techniques have shown that $CaHPO_4$ is triclinic[5] with space group $P\bar{1}$, and $CaHPO_4\cdot 2H_2O$ is monoclinic[6] with space group I 2/a. However, structure data on $SrHPO_4$ are both scarce and contradictory. For instance, de Schulten[7] claimed orthorhombic symmetry for $SrHPO_4$ while Bengtsson[8] in a more recent X-ray diffraction study of the monetites, found that $SrHPO_4$ was either monoclinic or triclinic.

We have discovered that $SrHPO_4$ may be precipitated from solution in two different crystalline modifications similar to the formation of the calcite and aragonite polymorphs of $CaCO_3$,[9] and we have designated these polymorphs as α-$SrHPO_4$ and β-$SrHPO_4$. In agreement with Ranby, *et al.*,[10] it has been shown that α-$SrHPO_4$ converts to β-

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[1] H. Bassett, *Z. anorg. Chem.*, **53**, 34, 49 (1907); **59**, 1 (1908); *J. Soc. Chem. Ind. (London)*, **28**, 722 (1910); *J. Chem. Soc.*, **111**, 620 (1917).

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[4] H. V. Tartar and J. R. Lorah, This Journal, **51**, 1091 (1929).

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[8] E. Bengtsson, *Arkiv Kemi Mineral. Geol.*, **15B**, 1 (1941).

[9] J. L. Wray and F. Daniels, This Journal, **79**, 2031 (1957).

[10] P. W. Ranby, D. H. Mash and S. T. Henderson, *Brit. J. App. Phys.*, Supplement #4, S18 (1955).