silicon tetrafluoride. The remaining beryllium sulfate was ignited to the oxide and the crucible weighed. The loss in weight gave the amount of SiO_2. The amounts of acids used gave no weighable residue. To check the procedure, an ignited, weighed sample of beryllium oxide was dissolved in hydrofluoric and sulfuric acids; the acids were fumed off and the residue reignited. The recovery of the beryllium oxide was quantitative.

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Reactions of Alkaline Earth Oxides. III. A Re-examination of the Hedvall Effect[1,2]

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The original experiments which are the basis of the postulate known as the Hedvall effect have been re-examined. It was found that the observed phenomena are not related to a phase transition as is generally supposed but appear to be the consequence of the formation of a liquid phase. The credibility of the Hedvall effect is discussed in the light of these and other data.

The increased reactivity of a solid during, and as a consequence of a crystallographic transformation, is known as the Hedvall effect.[4-9] This apparent behavior was first reported by Hedvall and Heuberger[10] who observed it in the course of the work with alkaline earth oxides which was previously discussed.[1,11] The original observations which were made on the reactions of BaO, SrO and CaO with $AgNO_3$ and Ag_2SO_4 are summarized in Table I. Today these data are still among the most widely quoted ones in support of the Hedvall rule.[4,6,9]

Table I lists the "reaction temperatures" of BaO, SrO and CaO with $AgNO_3$ and Ag_2SO_4. Phase transitions occur at 160 and 430° in $AgNO_3$ and Ag_2SO_4, respectively. Since it was thought that BaO, SrO and CaO have characteristic "reaction temperatures" of 345, 455 and 530°, respectively, the lowering of these values to those given in Table I was interpreted to be a consequence of the increased reactivity brought about by the transition in the silver salts.

TABLE I

Oxide	Reaction temp. with $AgNO_3$,[a] °C.	Reaction temp. with Ag_2SO_4,[b] °C.
BaO	170	342
SrO	172	422
CaO	164	422

[a] Transition temp., 160°. [b] Transition temp., 430°.

In previous work,[1] it was shown that the concept of a characteristic "reaction temperature" as applied to the alkaline earth oxides is ill-founded. The cited interpretation of the data in Table I, is, consequently, also questionable. The reactions of BaO, SrO and CaO with $AgNO_3$ and Ag_2SO_4 have, therefore, been re-examined.

Experimental

Two sets of experiments were performed: (1) differential thermal analysis of each reaction mixture and (2) direct microscopic examination of several reaction mixtures at temperatures in the neighborhood of the transition point. The purpose of the first is to reproduce the original experiments. Visual observation was expected to reveal what actually occurs at the transition point.

Differential thermal analyses were made with 50–50 mole per cent. mixtures of the reactants as well as with the pure materials under conditions previously described.[11] Microscopic examinations at elevated temperatures were performed at 60X with incident illumination on a Leitz microscope heating stage at atmospheric pressure in laboratory air. BaO, SrO and CaO were prepared as before.[1,11] Mallinckrodt analytical reagent grade $AgNO_3$ and Ag_2SO_4 were utilized without further treatment.

Results

The several DTA patterns are seen in Fig. 1. The sharp exotherm is in each case due to reaction to form the alkaline earth salt and Ag_2O or Ag^0. In the case of the reactions with $AgNO_3$, Ag_2O is formed first. With Ag_2SO_4, elemental silver is present after reaction. This was established by X-ray analysis of the samples immediately after occurrence of the exotherm.

The time between observed initiation and termination of reaction is of the order of one minute. This is in agreement with the comments of Hedvall who describe these as very rapid reactions. However, the "reaction temperatures" observed here are all above those listed in Table I. BaO and SrO are seen to react with $AgNO_3$ at a temperature close to the melting point of the latter. (Compare curves in Fig. 1.) Only the exotherm due to the reaction of CaO with $AgNO_3$ is observed to initiate below this temperature.

The reaction of Ag_2SO_4 with BaO as well as SrO is seen to "trigger-off" in the same manner and at the same temperature as the reactions of carbonates and other sulfates with these oxides.[11] The "reaction temperature" of Ag_2SO_4 + CaO is seen to correspond to the melting point of Ag_2SO_4.

$AgNO_3$ alone as well as the mixtures BaO-$AgNO_3$, SrO-$AgNO_3$ and CaO-$AgNO_3$ were observed on the

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(1) Part II, THIS JOURNAL, **82**, 355 (1960).

(2) Presented in part at the 136th National Meeting of the American Chemical Society, September, 1959, Atlantic City, N. J.

(3) Explosives Department, Experimental Station Laboratory, E. I. du Pont de Nemours & Co., Wilmington 98, Delaware.

(4) J. A. Hedvall, "Einführung in die Festkörperchemie," Fr. Vieweg and Son, Publishers, Braunschweig, 1952, p. 180ff.

(5) K. Hauffe, "Reaktionen in und an Festen Stoffen," Springer Publishing Co., Berlin, 1955, p. 628–629.

(6) G. Cohen, *Chem. Revs.*, **42**, 566 (1948).

(7) W. E. Garner, "Chemistry of the Solid State," Butterworth's Scientific Publications, London, 1955, p. 309.

(8) A. L. G. Rees, "Chemistry of the Defect Solid State," Methuen and Co., London, 1954, p. 91.

(9) T. J. Gray, Ed., "The Defect Solid State," Interscience Publishers, Inc., New York, N. Y., 1957, pp. 127–132.

(10) J. A. Hedvall and J. Heuberger, *Z. anorg. Chem.*, **128**, 1 (1923); **136**, 49 (1924).

(11) H. J. Borchardt and B. A. Thompson, THIS JOURNAL, **81**, 4182 (1959).

microscope hot stage. The temperature was raised at a rate of 10-15° per minute to about 130° and from there on at a rate of 1-2° per minute. With $AgNO_3$ alone the phase transformation was observed to be accompanied by a color change from water white to light orange. Melting was observed to occur at the reported melting point of 208°.

With the reaction mixtures it was possible to observe the phase transformation in $AgNO_3$ and reaction independently, the former being accompanied by the cited color change to light orange and the latter by the formation of black Ag_2O. In each case the phase transformation occurred without the slightest evidence of chemical reaction.

Formation of Ag_2O was only observed at higher temperatures; 190° with $CaO-AgNO_3$ and 208° in the cases of $BaO-AgNO_3$ and $SrO-AgNO_3$. In each case, a transparent melt was observed to form first. This turned black within a fraction of a second.

The mixture $CaO-AgNO_3$ was cycled through the transition point several times and then held above this temperature for 2 hr. No Ag_2O was seen to form under these circumstances either.

Discussion

Direct observation reveals that no Hedvall effect occurs in the reactions, $BaO-AgNO_3$, $SrO-AgNO_3$ and $CaO-AgNO_3$. In each case reaction occurred long after the phase transformation was complete, and then only when the temperature was raised to a point where a liquid phase formed. Although this does not, as such, prove that the reactions proceed *via* this phase, the unusual rate behavior observed with DTA strongly indicates that they do.[11] The origin of the liquid phase in the system $CaO-AgNO_3$ is not known.

Both BaO and SrO react with Ag_2SO_4 at a temperature where evidence for the formation of a liquid phase has previously been found.[11] Similarly, the melting of Ag_2SO_4 is seen to accompany the reaction with CaO.[12] Thus, the reactions in question cannot be cited as evidence for a Hedvall Effect. An explanation of this phenomenon, based on the formation of a liquid phase, was proposed by Balarew as early as 1924.[13]

These observations quite naturally raise the question whether there are grounds for believing that such an effect occurs at all. The answer to this question depends upon how one chooses to define "Hedvall Effect" there being an unfortunate ambiguity in the usage of this term. (Compare, for example, T. J. Gray, ref. 9, p. 112, 132.) As Hedvall originally conceived it, the effect refers only to the supposed increase in reactivity while a crystallographic transformation is actually taking place. Thus, the condition was imposed that the effect could only be observed if the time of reaction is of the same order as the time of transition. Alternately, it has been used in a more general sense to designate an increase in reaction rate near a transition point without the requirement of simultaneity. If one accepts Hedvall's original definition, then it appears that no valid evidence for the Hedvall rule has as yet been presented. Only a dozen or so reactions have been reported where anomalous behavior was observed at a transition point (many of these are described by Hedvall[4]). An examination of this literature reveals that the time of transformation was not determined in any of these cases.

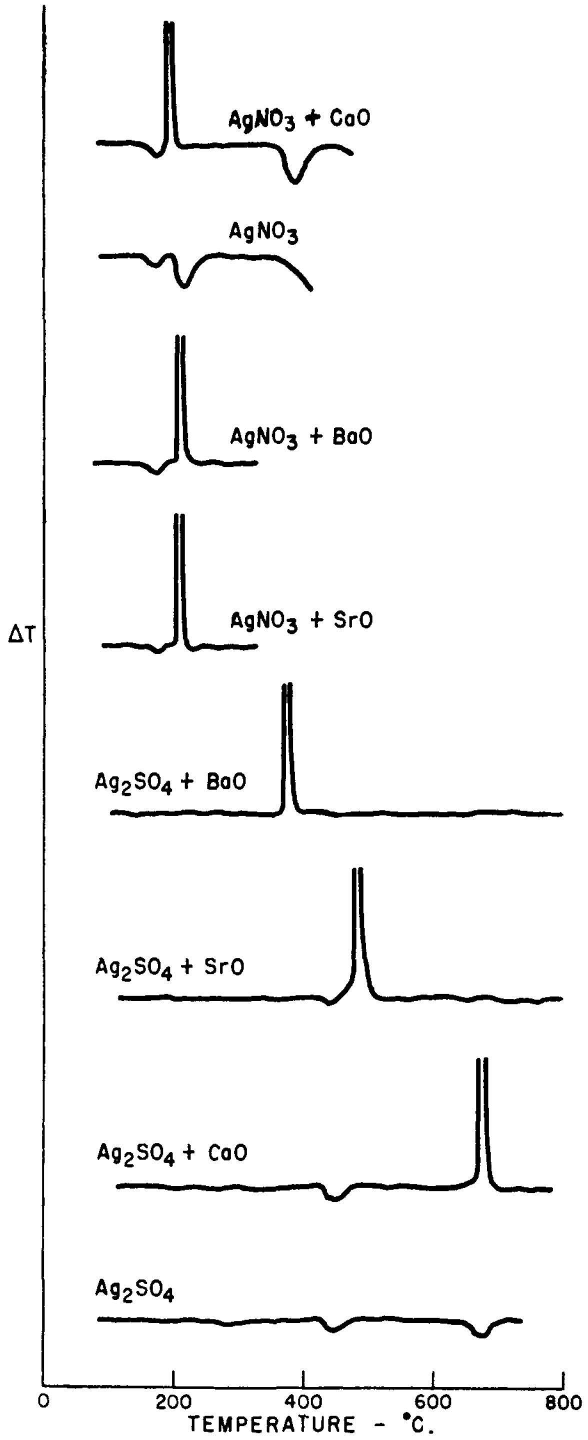

Fig. 1.—DTA patterns of materials indicated.

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(12) Rieman and Daniels (*J. Phys. Chem.*, **61**, 802 (1957)) have reported that CaO and Ag_2SO_4 react at temperatures as low as 500°. This finding, which has been qualitatively confirmed in our Laboratory, in no way conflicts with the comments above. A reaction must occur quite rapidly to be detectable by thermal or differential thermal methods. It is not until the temperature is in the neighborhood of the melting point of Ag_2SO_4 that the reaction rate is sufficiently rapid to give rise to measurable temperature increments.

(13) D. Balarew, *Z. anorg. Chem.*, **138**, 349 (1924).

As a matter of fact, none involve an attempt to observe the transformation and reaction independently. If the more general sense of the term is adopted, there is little question that such an effect occurs, although it most probably encompasses a whole class of phenomena, none of which are understood (see, for example, ref. 14).

(14) A. R. Ubbelohde, *Discussions Faraday Soc.*, **23**, 132 (1957).

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Studies on Ni(II) Complexes. I. Spectra of Tricyclic Schiff Base Complexes of Ni(II) and Cu(II)

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The relation between magnetism and stereochemistry is briefly summarized for complexes of quadricoördinate Ni(II) Complexes of the type Ni–O_2N_2 are seen especially likely to be distributed between planar spin-paired and spin-free forms. The spectra of a number of Ni(II) and Cu(II) complexes of the *cis* M–O_2N_2 type are reported. Ligand field strengths produced by salicylaldehyde- and acetylacetone-diimine ligand systems are compared, and it is shown that, as with the corresponding Cu(II) complexes, increase in the length of the methylene bridge is far more effective in weakening the ligand field than are ring substituents. The spectra of the Ni(II) complexes are discussed in relation to the singlet–triplet ground state separation and the ease of attaining partial paramagnetism in solution.

Introduction

The structures of complexes of quadricoördinate Ni(II) have been the subject of considerable discussion in recent years. Controversy has attended the assignment of tetrahedral stereochemistry to strictly four-coördinate complexes on the basis of their paramagnetism. This stereochemistry has been assigned in the past by many workers using the Pauling criterion for bond type,[1] which in the case of quadricoördinate Ni(II) states that paramagnetic complexes are $4s4p^3$ hybridized and tetrahedral whereas diamagnetic complexes are $4s3d4p^2$ bonded and planar. X-Ray structural determinations have been made on a number of diamagnetic four-coördinate complexes, such as potassium bis-(dithiooxalato) Ni(II),[2] Ni(II) phthalocyanine,[3] bis-(dimethylglyoxime) Ni(II),[4] bis-(salicylaldoxime) Ni(II),[5] dibromobis-(triethylphosphine) Ni(II),[6] bis-(salicylaldimine) Ni(II),[7] bis-(N-methylsalicylaldimine) Ni(II)[8] and all these have been shown to be planar. The increasing amount of structural information, recently summarized by Porai-Koshits,[9] emphasizes that many paramagnetic complexes once thought to be tetrahedral, *e.g.*, $Ni(en)_2(NCS)_2$,[10] Ni(tren)-$(NCS)_2$,[11] $Ni(py)_2(NCS)_2$,[12] bis(salicylaldehyde) Ni(II)·$2H_2O$,[13] are in reality effectively six-coördinate in the solid, thus accounting for their paramagnetism. Indeed, as is now well recognized, evidence for the existence of discrete tetrahedral Ni(II) complexes is scant. Only recently has definite evidence been brought forth in the form of spectral, magnetic and dipole moment data to verify the existence of this class of complexes. The complexes $Ni[(C_6H_5)_3P]_2X_2$ ($X = Cl^-, Br^-, I^-, NO_3^-$) examined by Venanzi,[14] and $[(C_6H_5)_3AsCH_3]_2NiX_4$ ($X = Cl^-, Br^-, I^-$) studied by Nyholm[15a] and $Ni[(C_6H_5)_3MO]_2X_2$ ($M = P$, $X = Cl^-, Br^-, I^-$; $M = As$, $X = Cl^-, Br^-$) recently prepared by Cotton and Goodgame[15b] are almost certainly tetrahedral or pseudo-tetrahedral (C_{2v}).

The question remains as to the structures of other paramagnetic apparently four-coördinate (anhydrous) Ni(II) complexes of 8-hydroxyquinoline, *o*-hydroxyacetophenone, formylcamphor, anthranilic acid, acetylacetone,[16] salicylaldehyde,[16] and many others, all of which have magnetic moments in the range 3.0–3.3 B.M. Spin-free quadricoördinate complexes such as these have been little investigated, and there is no convincing evidence of any sort that any of these complexes are tetrahedral either in solution or in the solid. The same may be said for complexes paramagnetic in solution yet diamagnetic as solids.[17,18] It has been pointed out on several occasions[19,20] that quad-

(1) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1948, pp. 112 ff.

(2) E. G. Cox, W. Wardlaw and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

(3) J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(4) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

(5) L. L. Merritt, Jr., C. Guare and A. E. Lessor, Jr., *ibid.*, **9**, 253 (1956).

(6) G. Giacometti, V. Scatturin and A. Turco, *Gazz. chim. ital.*, **88**, 434 (1958).

(7) J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, **12**, 842 (1959).

(8) E. Frasson, C. Panattoni and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(9) M. A. Porai-Koshits, *Russ. J. Inorg. Chem.* (Eng. trans.), **4**, 332 (1959).

(10) E. C. Lingafelter, *Nature*, **182**, 1730 (1958).

(11) S. E. Rasmussen, *Acta Chem. Scand.*, **13**, 2009 (1959).

(12) M. A. Porai-Koshits and G. N. Tishchenko, *Kristallografiya*, **4**, 239 (1959).

(13) E. C. Lingafelter, J. D. Breazeale, J. M. Stewart, Abstr. 4th 1UC Int. Conf., Montreal, 1957, p. 56.

(14) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

(15) (a) N. S. Gill, P. Pauling and R. S. Nyholm, *Nature*, **182**, 168 (1958); N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959). (b) F. A. Cotton and D. M. L. Goodgame, THIS JOURNAL, in press.

(16) Bis-(acetylacetonato) Ni(II) and bis-(salicylaldehyde) Ni(II) are probably not strictly four-coördinate. Preliminary X-ray studies [*cf.* G. J. Bullen, *Nature*, **177**, 537 (1956) and F. K. C. Lyle, B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **12**, 938 (1959)] have indicated that, especially with the acetylacetonate, trimeric structures may exist in the solid.

(17) H. S. French, M. Z. Magee and E. Sheffield, THIS JOURNAL, **64**, 1924 (1942); B. Willis and D. P. Mellor, *ibid.*, **69**, 1237 (1947); F. Basolo and W. R. Matoush, *ibid.*, **75**, 5663 (1953); H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 3431 (1955); S. Fujii and M. Sumitani, *Sci. Rpts. Tohoku Univ.*, (Ser. 1) **37**, 49 (1953).

(18) L. Sacconi, P. Paoletti and G. Del Re, THIS JOURNAL, **79**, 4092 (1957); L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *ibid.*, **82**, 3487 (1960).

(19) C. J. Ballhausen, *Kgl. Danske. Vid. Mat. phys. Medd.*, **29**, No. 9 (1955).

(20) C. J. Ballhausen and A. D. Liehr, THIS JOURNAL, **81**, 538 (1959).