

The *trans*-compound was eluted with 450 ml. of anhydrous alcohol-ether (1:1) and the *cis*-isomer with 250 ml. of dry ether. The solvents were removed *in vacuo*.

The *trans*-oxime appeared as an oil and was crystallized by dissolving it in about 50 ml. of benzene at 25° and scratching. The yield was 1.9 g.; the colorless, short, quadrangular plates melted at 125.5°. The *cis*-compound came out in the form of crystals which contained ether. These were dissolved in 6 ml. of acetone at room temperature and rapidly evaporated with a carbon dioxide stream at 25°. The oily residue was evaporated with 2 ml. of benzene, dissolved in 10 ml. of cold benzene and scratched. Thin, elongated, colorless prisms appeared (1.2 g., m. p. 121-122°).

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>O<sub>4</sub>N: N, 4.88. Found: (*cis*) N, 5.08; (*trans*) N, 4.99.

The difference in the melting points of the two isomers is remarkably small. The configurations, however, are given by the location on the column and by the color reactions. Chromatography showed the presence of less than 1% of the *cis*-compound in the *trans*-sample and *vice versa*.

(a) A mixture of 75 mg. of each isomer was dissolved in 35 ml. of benzene by slight warming, developed on a column (14 × 1.7 cm.) with 50 ml. of benzene containing 3% abs. alcohol, and brushed:

10 sky blue (empty top section)  
24 dark green (*trans*-anisoin oxime)  
37 blue (interzone)  
7 dark brown (*cis*-anisoin oxime)  
65 sky blue (bottom section containing a faint yellow line)

After elution with 55 ml. of the solvent mentioned, 69.2 mg. of *trans*-oxime (m. p. 125-125.5°, after crystallization from cold benzene) and 68.3 mg. of *cis*-oxime (m. p. 122.5-123.5°, after crystallization) were isolated, the total recovery being 92%. The interzone yielded 0.8 mg. of the *trans*-compound.

(b) It was found in similar adsorption experiments that 1.6 mg. of *cis*-anisoin oxime can be detected in the presence of 200 mg. of the *trans*-isomer or 1.2 mg. of *trans*- in the presence of 135 mg. of the *cis*-compound. The limit is 0.5-1%.

(c) A solution of 140 mg. of *cis*-anisoin oxime in 40 ml. of ethyl alcohol was refluxed for one and one-half hours. After removing the solvent and chromatographing as described in expt. (a), a 6-mm. zone was located above the main zone by brushing. This contained 11.5 mg. (8%) of the *trans*-compound, formed by isomerization. A parallel experiment carried out with *trans*-anisoin oxime yielded 2.5% of formed *cis*-isomer.

(d) A solution of 125 mg. of pure *cis*-anisoin oxime in 30 ml. of benzene was developed in three and one-fourth hours on a column (17.5 × 1 cm.) with 50 ml. of benzene containing 3% absolute alcohol. From the interzone 13.7 mg. of the *trans*-isomer was isolated. The extent of the "column isomerization" amounted to 11% in this case while the corresponding figure for a short experiment is about 1%.

### Summary

The chromatographic brush method, with an ammoniacal copper solution as color reagent, has been used for the detection and separation of *cis*- and *trans*-benzoin and anisoin oximes on Neutrol Filtrol columns. In a mixture composed of two stereoisomers, 1-2% of either form can be rapidly detected in the presence of the other. Some data concerning the interconversion of stereoisomeric oximes are given, and the influence of the adsorbent on the *cis-trans* shift is discussed.

PASADENA, CALIFORNIA

RECEIVED MAY 18, 1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

## The Configuration of Organic Coordination Compounds of Nickel, with Especial Reference to Bis-formylcamphor-ethylenediamine-nickel

BY H. S. FRENCH, M. Z. MAGEE<sup>1</sup> AND E. SHEFFIELD<sup>1</sup>

Evidence is accumulating from various groups of investigators which may ultimately furnish an answer to the question implied in Pauling's<sup>2</sup> statement that "factors which determine whether the diamagnetic square or the paramagnetic tetrahedral configurations will be assumed by a nickel complex cannot be stated precisely." The present paper seeks to add to the evidence results of three different types: first, the magnetic susceptibilities of nine compounds; second, the absorption spectra of four of these compounds; and third, the

*relation between* the adsorption spectrum and rotatory dispersion of a single one of the compounds.

**Magnetic Susceptibility.**—Determination of magnetic susceptibility is probably the most generally used method for the study of the configuration of the quadricovalent nickel complexes, since diamagnetism is associated with the square coplanar configuration and no unpaired electrons, while paramagnetism is associated with the tetrahedral configuration and two unpaired electrons. Pauling<sup>3</sup> has given the most satisfactory explanation for this change in the number

(1) Taken in part from the M.A. Thesis of M. Z. Magee and from the Honors Thesis of E. Sheffield.

(2) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 112.

(3) Pauling, *ibid.*, p. 111.

of unpaired electrons by his theory of the hybridization of bond orbitals. The nine compounds chosen for this study of magnetic susceptibility are the following

(I) bis-salicylaldehyde nickel  $(C_6H_4(CHO)O)_2Ni$

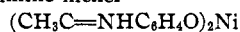
(II) bis-*o*-hydroxyacetophenone nickel



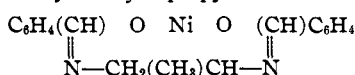
(III) bis-formylcamphor nickel  $(C_{10}H_{14}(CHO)O)_2Ni$

(IV) bis-salicylaldehyde nickel  $(C_6H_4(CH=NH)O)_2Ni$

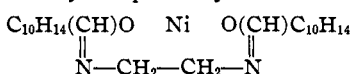
(V) bis-*o*-hydroxyacetophenoneimine nickel



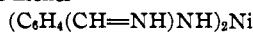
(VI) bis-salicylaldehyde-propylenediamine nickel



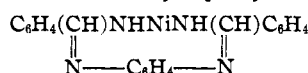
(VII) bis-formyl camphor ethylenediamine nickel



(VIII) bis-*o*-aminobenzalimine nickel



(IX) bis-*o*-aminobenzaldehyde phenylenediamine nickel



Since no new methods of preparation were used for any of the compounds studied, we refer to the original directions by footnotes in Table I. We include also in Table I, the results of the analyses for nickel, and of the magnetic susceptibility determinations. Magnetic susceptibilities were

TABLE I

| Compound            | Calcd. % Ni | Found % Ni | $\chi_{mol} \times 10^6$ | $\mu$ |
|---------------------|-------------|------------|--------------------------|-------|
| A I <sup>a,b</sup>  | 17.43       | 17.47      | 4265                     | 3.2   |
| II <sup>c</sup>     | 12.06       | 11.97      | 3884                     | 3.1   |
| III <sup>d</sup>    | 12.96       | 12.94      | 4857                     | 3.4   |
| B IV <sup>a</sup>   | 19.65       | 19.69      | Diamagnetic              |       |
| V <sup>c</sup>      | 17.96       | 17.84      | Diamagnetic              |       |
| VI <sup>e</sup>     | 17.33       | 17.27      | Diamagnetic              |       |
| VII <sup>f</sup>    | 13.31       | 13.27      | 1522                     | 1.9   |
| (diamagnetic solid) |             |            |                          |       |
| C VIII <sup>g</sup> | 19.87       | 19.68      | Diamagnetic              |       |
| IX <sup>g</sup>     | 15.83       | 15.61      | Diamagnetic              |       |

<sup>a</sup> Adams and Tyson, *THIS JOURNAL*, **62**, 1228 (1940). Their values for %Ni,  $\chi_m \times 10^6$ , and  $\mu$  are 17.53, 3851, and 3.1 for I, and 19.70, diamagnetic for IV.

<sup>b</sup> Mellor and Craig, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 478 (1941). Their values for  $\chi_m \times 10^6$  and  $\mu$  are 4230 and 3.2 for I.

<sup>c</sup> Pfeiffer, Buchholz and Bauer, *J. prakt. Chem.*, **129**, 172 (1931).

<sup>d</sup> French and Corbett, *THIS JOURNAL*, **62**, 3221 (1940).

<sup>e</sup> Pfeiffer, Hesse, Pfitzner, Scholl and Thielert, *J. prakt. Chem.*, **149**, 255 (1937).

<sup>f</sup> Pfeiffer, Christelheit, Hesse, Pfitzner and Thielert, *ibid.*, **150**, 261 (1938).

<sup>g</sup> Pfeiffer, Breith, Lübke and Tsumaki, *Ann.*, **503**, 101 (1933).

measured by the Gouy<sup>4</sup> method and from these the magnetic moments in Bohr magnetons were calculated in the usual way.<sup>5</sup> The analyses for nickel were carried out on the micro-scale by igniting the compound to the oxides of nickel, and reducing the oxides to nickel in a stream of hydrogen.

**Absorption Spectra.**—The absorption spectra of the two pairs of compounds, I and VI, III<sup>d</sup> and VII were investigated in both the visible and ultraviolet regions. The method used in the ultraviolet region is the same as in previous com-

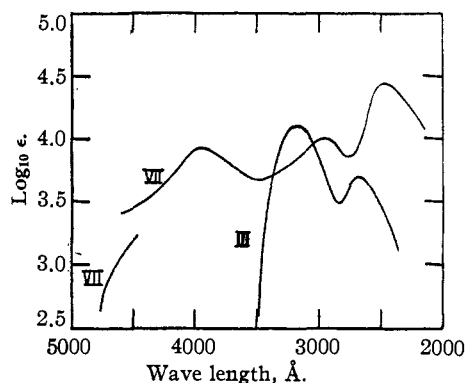


Fig. 1.—Curve III: absorption spectrum of bis-formyl camphor nickel in methyl alcohol<sup>d</sup>; curve VII, absorption spectrum of bis-formyl camphor ethylenediamine nickel in methyl alcohol.

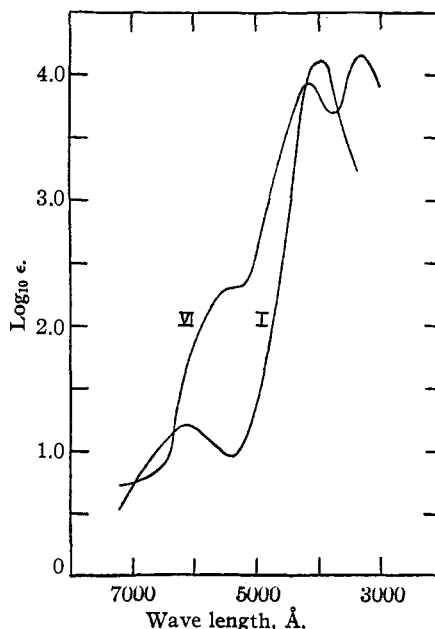


Fig. 2.—Curve I, absorption spectrum of bis-salicylaldehyde nickel in pyridine; curve VI, absorption spectrum of bis-salicylaldehyde propylenediamine nickel in pyridine.

(4) Gouy, *Compt. rend.*, **109**, 935 (1889).

(5) Pauling, *loc. cit.*, pp. 105–106.

munications from this Laboratory.<sup>d</sup> The method used in the visible region has already been described.<sup>6</sup> The results are shown in Figs. 1, 2 and curve AB in Fig. 3.

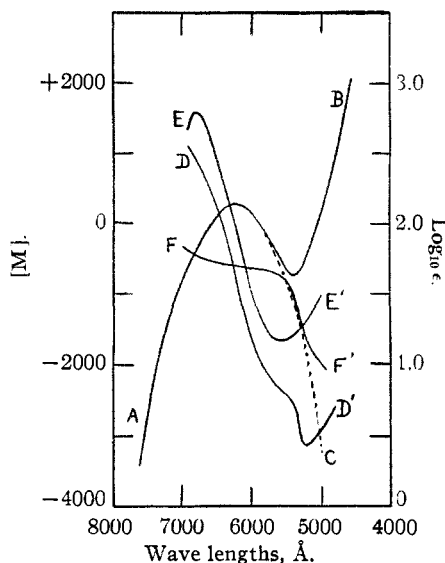


Fig. 3.—Bis-formyl camphor ethylenediamine nickel: AB, observed absorption spectrum; AC, calculated absorption band; DD', observed rotatory dispersion'; EE', calculated rotatory dispersion; FF', residual rotatory dispersion.

**Analysis of Rotatory Dispersion and Absorption Spectra.**—Our third method of investigation was described in detail in a recent communication<sup>d</sup> from this Laboratory. This method has now been applied to compound VII. The experimental rotatory dispersion curve is drawn from Pfeiffer's<sup>f</sup> data. The absorption spectrum in both the visible and ultraviolet regions is here shown for the first time.<sup>7</sup> The results of the analysis are shown in Fig. 3 and in Tables II, III and IV.

TABLE II

| CALCULATED POINTS FOR THE THEORETICAL ABSORPTION BAND OF BIS-FORMYLCAMPHOR-ETHYLENEDIAMINE-NICKEL         |      |                            |           |                            |
|---|------|----------------------------|-----------|----------------------------|
| $(\text{Log}_{10} \epsilon)_{\text{max.}} = 2.13$ at $6250 \text{ \AA.}$ ; $\theta = 654.55 \text{ \AA.}$ |      |                            |           |                            |
| $\lambda$   |      | $\text{Log}_{10} \epsilon$ | $\lambda$ | $\text{Log}_{10} \epsilon$ |
| 6250  |      | 2.13                       | 6750      | 5750                       |
| 6300  | 6200 | 2.12                       | 7000      | 5500                       |
| 6400  | 6100 | 2.11                       | 7250      | 5250                       |
| 6500  | 6000 | 2.07                       | 7500      | 5000                       |

### Discussion

Mellor and Craig<sup>b</sup> have suggested a useful classification of nickel compounds according merely to the four atoms joined to the nickel.

(6) French and Lowry, *Proc. Roy. Soc. (London)*, **106A**, 511 (1924).

(7) Mills and Mellor, *THIS JOURNAL*, **64**, 181 (1942), mention a general maximum for such compounds at  $385 \text{ m}\mu$ , but give no further details.

TABLE III

CALCULATED POINTS FOR THE ROTATORY DISPERSION GOVERNED BY THE ABSORPTION BAND AT  $6250 \text{ \AA.}$  OF BIS-FORMYLCAMPHOR-ETHYLENEDIAMINE-NICKEL

| $\lambda$ | [M]   | $\lambda$ | [M]   |
|-----------|-------|-----------|-------|
| 6900      | 1485  | 5750      | -1576 |
| 6750      | 1520  | 5600      | -1659 |
| 6600      | 1293  | 5500      | -1621 |
| 6400      | 702   | 5300      | -1414 |
| 6250      | 0     | 5150      | -1227 |
| 6100      | -579  | 5000      | -1056 |
| 5900      | -1284 |           |       |

TABLE IV

CALCULATED POINTS FOR THE RESIDUAL ROTATORY DISPERSION OF BIS-FORMYLCAMPHOR-ETHYLENEDIAMINE-NICKEL

| [M]  | $\lambda$ | $1/[\text{M}]$         | $\lambda^2$         |
|------|-----------|------------------------|---------------------|
| -480 | 6800      | $20.83 \times 10^{-4}$ | $46.24 \times 10^6$ |
| 520  | 6600      | 19.23                  | 43.55               |
| 550  | 6400      | 18.18                  | 40.97               |
| 600  | 6200      | 16.66                  | 38.49               |
| 620  | 6000      | 16.13                  | 36.00               |
| 650  | 5800      | 15.40                  | 33.64               |
| 720  | 5600      | 12.90                  | 31.37               |
| 840  | 5500      | 11.90                  | 30.25               |
| 1090 | 5400      | 9.18                   | 29.16               |
| 1350 | 5300      | 7.41                   | 28.09               |
| 1640 | 5200      | 6.10                   | 27.04               |
| 1960 | 5000      | 5.10                   | 25.00               |

We believe that it will be necessary in any final interpretation to subdivide these classes according to the chelate rings involved, as suggested by Diehl<sup>8</sup> or by Pfeiffer.<sup>9</sup> Our compounds I, II and III fall under Mellor and Craig's class A, in which nickel is joined to four oxygen atoms. Table I shows paramagnetic susceptibility for all three compounds, corresponding to two unpaired electrons and tetrahedral configuration. So far as we know, all class A compounds studied by other investigators are also paramagnetic. Class B includes compounds in which nickel is joined to two oxygen and two nitrogen atoms and it is in such compounds that previous investigators have failed to find any uniformity in magnetic susceptibility. Our compounds IV, V, VI and VII fall in this class. Table I shows diamagnetic susceptibility for all four compounds, corresponding to no unpaired electrons and square co-planar configuration. Compound VII offers the interesting peculiarity, however, that it is diamagnetic in the solid state, but paramagnetic in methyl alcohol solution. This peculiarity will be discussed later. Class C includes compounds in which nickel is joined to four nitrogen atoms. Table I shows our compounds VIII and IX in this

(8) Diehl, *Chem. Rev.*, **21**, 39-42 (1937).

(9) Pfeiffer, *Z. angew. Chem.*, **63**, 93-98 (1940).

class to be diamagnetic, and this fact is in accord with the results of other investigators for compounds in class C.

The absorption spectra studies have thus far been applied to too limited a number of compounds for reliable generalizations. In the four curves shown here it may be noted that the change of two oxygen atoms to two nitrogen atoms in otherwise similar nickel complexes has in each case (1) increased the number of absorption maxima, (2) moved the ultraviolet maxima to longer wave lengths, and (3) moved the visible maximum to shorter wave lengths. The last two effects result in the long-wave length bands approaching each other so closely that one may become merely a step-out in the nitrogen-containing complex. It must remain for further investigation to prove whether *many* absorption bands, including one poorly defined step-out, are always characteristic of diamagnetic, square co-planar nickel complexes, and whether such a phenomenon may serve as one criterion for configuration. Incidentally, it should be added that the substitution of nitrogen for oxygen in metallic coördination compounds frequently moves the visible absorption band characteristic of the metal to shorter wave lengths,<sup>10</sup> and also that the formation of a Schiff base from an ortho (or para) hydroxy aldehyde or ketone causes an additional band to appear in the absorption spectrum.<sup>11</sup> In general, the color in the solid state of the nitrogen-containing compounds of class B is reddish or yellowish, while that of the paramagnetic compounds of class A is green or blue.<sup>7</sup> The few exceptions to this statement thus far found emphasize the necessity for the complete absorption spectra investigations, which alone can show the responsibility for the apparent color being borne by the usual *two* nickel absorption bands.<sup>12</sup>

An earlier paper<sup>d</sup> from this Laboratory has already shown by the method of rotatory dispersion analysis that the nickel center in compound III (class A) has the tetrahedral configuration. The argument was there based on the fact that the rotatory dispersion of the molecule was governed almost entirely by the absorption band of the

nickel center, and that only the tetrahedral nickel configuration could result in optical activity. The conclusion was confirmed by finding the compound strongly paramagnetic.

This method has now been applied to compound VII (class B). We find that a logical analysis of the rotatory dispersion (Fig. 3) is given by attributing a considerable degree of optical activity to the absorption band at 6250 Å., due to the nickel center of the molecule. Only by such an assumption is a curve of residual rotation obtained with no inflection within that absorption band. We have already noted that this compound is paramagnetic in methyl alcohol solution, and this fact confirms the conclusion from the rotational dispersion and absorption spectrum. Yet, in the solid state it is diamagnetic. Mellor and Craig<sup>b</sup> suggest two conditions for paramagnetism in class B: first, that the oxygen atom joined to the nickel was *not* previously an hydroxyl oxygen; second, that even if the oxygen atom was previously an hydroxyl oxygen (as in their bis-8-hydroxy-quinoline nickel and presumably in our tautomeric compound) steric effects function to force the bonds out of coplanar positions. Porter<sup>13</sup> similarly explains the unexpected paramagnetism of the nickel complex of 3,3',5,5'-tetramethylpyrromethane-4,4'-dicarboxylate by steric interference of the substituted groups. Pfeiffer<sup>9</sup> states that only a slight displacement of the four bonds out of the plane is enough to give asymmetry of the metallic center. In our bis-formyl camphor ethylenediamine nickel the oxygen atoms joined to the nickel were at least in an enolic hydroxyl group, so that diamagnetism would be expected. The presence of the ethylenediamine ring would tend to preserve the coplanarity of the molecule rather than force the bonds toward the tetrahedral configuration. A determining factor working in the opposite direction, however, is the presence of asymmetric centers in the camphor rings. That such an asymmetric center induces asymmetry in the carbonyl group of camphor was shown by Kuhn and Gore<sup>14</sup> and is explained by Kuhn's<sup>15</sup> vicinal effect. Such induction might easily go further, after rendering the aldimine bonds asymmetric and cause sufficient strain at the nickel center for the slight "twist" necessary for asymmetry (and ionization ultimately). Such "twist" might not occur in the solid state (hence diamagnetism) but

(10) French and Lowry, *Proc. Roy. Soc. (London)*, **106**, 502 (1924).

(11) This conclusion is drawn from a study of the absorption spectra of Schiff bases from Varga, *Magyar Chem. Folyoirat*, **45**, 83 (1939).

(12) Datta and Deb, *Phil. Mag.*, **20**, 1121 (1935); Bäckström, *Arkiv. Kemi. Mineral. Geol.*, **13A**, No. 24, 16 (1940); Bhagwat, *J. Indian Chem. Soc.*, **17**, 53 (1940).

(13) Porter, *J. Chem. Soc.*, 368 (1938).

(14) Kuhn and Gore, *Z. physik. Chem.*, **12**, 389 (1931).

(15) Kuhn and Braun, *ibid.*, **8**, 281 (1930).

might be made possible under the influence of the solvent methyl alcohol. The fact that the change is not complete but that an equilibrium exists in methyl alcohol is indicated both (1) by the low value of the magnetic susceptibility and (2) by the effect of dilution on the absorption spectrum, especially in the region governed by the nickel aldimine complex band (step-out) at about 4500 Å.

We might go further and suggest that this equilibrium in methyl alcohol solution consists of approximately one-third of the paramagnetic form and two-thirds of the diamagnetic form of the molecules, since the observed value of the magnetic susceptibility is approximately one-third as great as the value to be expected for a paramagnetic compound of this type.

Confirmation of the interpretation just given for our results comes from further consideration of the curve for residual rotatory dispersion. When the values of  $1/M$  are plotted against  $\lambda^2$  for this curve, the points do not yet lie on a straight line, showing that at least two other absorption bands are optically active. It is possible, but not advisable without further experimental data, to analyze further the residual curve into two others, one governed by the band at 4500, due probably to the nickel aldimine complex, and the second by the far distant band of the camphor radical itself.

### Summary

New data are presented on the visible and ultraviolet absorption spectrum of the nickel complex of formylcamphor-ethylenediamine and on its magnetic susceptibility in the solid state and in methyl alcohol solution. From an analysis of the relation between its rotatory dispersion and its absorption spectrum, and from the magnetic susceptibilities, the conclusion is drawn that the configuration of the nickel complex is square coplanar in the solid state, but strained and twisted under the influence of the asymmetric camphor to such an extent that the nickel center in methyl alcohol solution also is asymmetric and tends toward the tetrahedral configuration. New data are also presented for the magnetic susceptibilities of five other organic coordination compounds of nickel: with *o*-hydroxyacetophenone, *o*-hydroxyacetophenone imine, salicylic aldehyde propylenediamine, *o*-amino-benzalimine, and *o*-aminobenzaldehyde phenylenediamine. New data are given for the absorption spectra in the visible and ultraviolet of bis-salicylaldehyde nickel and bis-salicylaldehyde-propylenediamine-nickel. Tentative conclusions are drawn concerning the difference in absorption spectra of paramagnetic and diamagnetic compounds of the types studied.

WELLESLEY, MASS.

RECEIVED MARCH 27, 1942

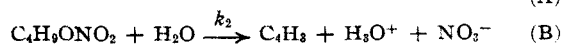
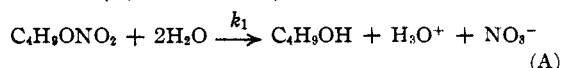
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## Rate and Mechanism in the Reactions of *t*-Butyl Nitrate and of Benzyl Nitrate with Water and with Hydroxyl Ion<sup>1</sup>

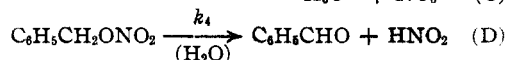
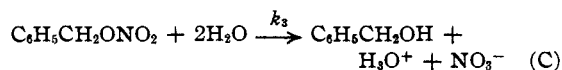
BY GLENNARD R. LUCAS AND LOUIS P. HAMMETT

We have investigated kinetically the reactions with water and hydroxyl ion of two alkyl nitrates which illustrate the two kinds of reactions other than hydrolysis which such substances undergo in the presence of water.<sup>2</sup>

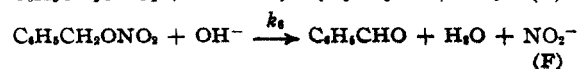
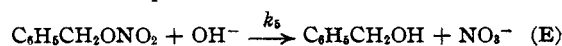
In the case of tertiary butyl nitrate the only reactions are the two solvolytic ones producing alcohol (A) and olefin (B).



In the case of benzyl nitrate no olefin is produced but the solvolysis to benzyl alcohol and nitric acid (C) is accompanied by a likewise first order formation of benzaldehyde and nitrous acid (D).



These first order reactions are accompanied by second order reactions with hydroxyl ion leading to the same products.



(1) Dissertation submitted by Glennard Ralph Lucas in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

(2) Klason and Carlson, *Ber.*, **39**, 2752 (1906); **40**, 4183 (1907); Carlson, *ibid.*, **40**, 4191 (1907).