but when applied to all the data, all self-consistent approaches had definite shortcomings. Undoubtedly, the exact interplay of all the Rydberg structure and the various intensity patterns is complex.

There is currently additional interest in the photoelectron spectra of these compounds.[15-17] Sometimes useful correlations can be discerned when one compares the photoelectron and optical spectra. Certain major intensity correlations can be naively drawn between the two sets of data and may suggest sources of intensity. For example, in the optical spectrum of CCl_4, one sees basically three large groups of intensity (disregarding the weaker first transition). The centers of these intensity groups are separated by roughly 7 kK, with the middle member being the most intense and showing doublet structure. The photoelectron spectrum shows the same structural pattern, again with the separations of the three major intensity groups being about 7 kK and the middle member showing some structure. Also, in $CHCl_3$, the major intensity pattern of the photoelectron data is again three major bands of intensity with the middle being most intense. This pattern is repeated in the optical spectrum of $CHCl_3$. While no one-to-one correspondence is intended, it is suggested that transitions involving electrons other than just the highest filled orbital electrons may be playing a part in the overall intensity distribution in the optical spectra. For example, it seems certain that the σ electrons in the C–Cl bond must be considered. More work needs to be done before such correlations are understood, and efforts are being made in those directions.

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Ambident Behavior of Nitrite Ion. Reactions of 2,4-Dinitrohalobenzenes and 1,2,4-Trinitrobenzene with Sodium Nitrite[1]

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Abstract: The reaction of sodium nitrite in aqueous acetonitrile (3:2) at pH 7 and 25° with the four 2,4-dinitrohalobenzenes clearly demonstrates the ambident nature of the nitrite ion. The relative importance of the two modes of displacement, O attack and N attack, depends on the halogen displaced, oxygen attack increasing with increasing electronegativity of the halogen. Dinitrofluorobenzene reacts totally by O attack, whereas dinitroiodobenzene reacts altogether by N attack. Dinitrochloro- and dinitrobromobenzene demonstrate both modes of displacement. The rates of oxygen and nitrogen attack by nitrite ion were determined for each of the 2,4-dinitrohalobenzenes, and the rate of oxygen attack was determined for 1,2,4-trinitrobenzene.

Nitrite ion has two potential reaction sites.[2] In 1955, Kornblum[3] coined the term "ambident anions" to describe species having multiple reaction sites. Gompper[4] preferred to speak of "ambifunctional nucleophilic compounds." The ambident nature of nitrite ion in organic metal complexes is well documented.[5] Complexes with both nitro and nitrito linkages are known, some having both linkages in the same complex. The type of bond appears to be dependent on the electronic structure of the metal and the steric requirements imposed by other ligands. Evidence exists for nitro–nitrito equilibria in some complexes,[5] and a number of nitro-coordinated compounds are prepared from their nitrito isomers that have formed initially as unstable intermediates.

Also well documented[3] is the nitrite ion reaction with alkyl halides to give a mixture of alkyl nitrites and nitroalkanes. The relative amounts of these products, resulting from oxygen and nitrogen attack, respectively, depend on many factors: cation, halide, solvent, temperature, and alkyl structure. The reaction of silver nitrite with para-substituted benzyl bromides showed that *p*-methoxybenzyl bromide gives a greater ratio of nitrite ester to nitro compound than does *p*-nitrobenzyl bromide. Kornblum concluded that the greater the carbonium ion like character of the halogen compound in the transition state, the more likely the nitrite ion is to attack through the oxygen atom. With the strongly positive center of a carbonium ion like species, the reaction is controlled by electrostatic attraction to the more electronegative oxygen atoms. When

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(1) Presented before the Division of Organic Chemistry at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract ORGN-53.

(2) V. Meyer and O. Stuber, *Chem. Ber.*, **5**, 203 (1872).

(3) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6269 (1955).

(4) R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **3**, 560 (1964).

(5) A. H. Norbury and A. L. P. Sivha, *Quart. Rev., Chem. Soc.*, **24**, 69 (1970).

the positive charge is less important, the more nucleophilic nitrogen atom predominates to form nitro compounds. Pearson and Songstad[6] give essentially the same explanation in terms of their hard–soft acid–base theory.

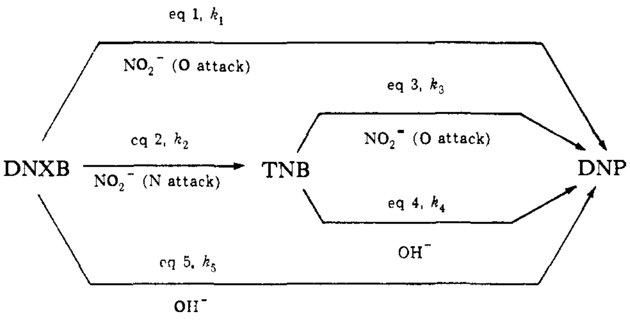
The ambident behavior of alkali metal and silver salts of 2-pyridone toward alkyl halides[7] is also consistent with Kornblum's proposal that silver ion favors the alkylation of 2-pyridone at the more electronegative oxygen atom.

The reaction[8] of *o*-dinitrobenzene with tervalent phosphorus compounds such as triethyl phosphite supports Kornblum's generalizations. The nucleophilic phosphorus displaces a nitro group to form an intermediate phosphonium nitrite. The oxygen atom of the nitrite ion then attacks an α carbon to give diethyl *o*-nitrophenyl phosphonate and ethyl nitrite. Nitroalkane is absent because the transition state for nitrite attack is strongly influenced by the phosphonium component and must be carbonium like.

Although nitrite reactions with aliphatic halogen systems have been much studied, little work has been done with aromatic halogen compounds. This may be due to the instability of aryl nitrite esters. In 1934, Ringeissen[9] permitted 1-chloro- and 1-bromo-2-naphthol to react with silver nitrite and obtained a small amount of 1-nitro-2-naphthol. More recently, Dokunikhin, *et al.*,[10] found that sodium nitrite reacts with 2,3,6,7-tetrachloroanthraquinone in *N*,*N*-dimethylformamide to yield isomeric β-dinitro-β-dihydroxyanthraquinones, demonstrating that aryl halide reactions can be affected by the ambident nature of the nitrite ion.

The present study developed from an investigation of the nucleophilicity of the nitrite ion toward 2,4-dinitrochlorobenzene (DNClB) in 40% acetonitrile–60% water at 25° and pH 7. We observed that the rate at which the product, 2,4-dinitrophenol (DNP), formed underwent a 25-fold rate acceleration during the first 20% of the reaction. This acceleration was the first clue that the nitrite ion was behaving in an ambident manner. Scheme I shows the possible reaction paths from 2,4-dinitrohalobenzene (DNXB) to DNP. Aside from the hydroxide reactions, which are negligible at pH 7, the phenol is formed *via* O-attack by nitrite ion on both the halobenzene and the intermediate 1,2,4-trinitrobenzene; *the initially formed nitrite ester is so rapidly hydrolyzed to phenoxide by the medium that the ester has no kinetic significance.* 1,2,4-Trinitrobenzene (TNB) arises from N attack by nitrite ion on DNXB. Rate accelerations were found when the halogen was chlorine, bromine, and iodine, whereas 2,4-dinitrofluorobenzene (DNFB) reacted with nitrite only as indicated by eq 1.

Scheme I



Experimental Results

Product Identification. The intermediate, TNB, was found in the reacting solutions of the first three DNXB's by gas chromatography. Further identification was made by mass spectrometry following the isolation of TNB from a solution of DNClB and sodium nitrite. DNP was identified by thin layer chromatography using silica gel G and 1:1 benzene–chloroform; the product matched the R_f value of a pure sample of DNP. Although there were five simultaneous reactions involved in producing DNP, each rate constant could be measured and the ambident behavior of nitrite toward each DNXB determined.

Spectrophotometric Method. Reactions between DNXB's or TNB and sodium nitrite were carried out in 40% acetonitrile–60% water buffered with 0.025 *M* phosphate, pH 7, at 25°. The concentration of DNXB or TNB was 10^{-2} *M*; that of $NaNO_2$ was 0.40 *M*.

Gas Chromatographic Method. Gas–liquid chromatography was used to measure the concentrations of both DNXB and TNB in solutions of 40% acetonitrile–60% water having initial concentrations of 10^{-2} *M* DNXB, 0.40 *M* sodium nitrite, and 0.02 *M* phosphate buffer at 25°. Each 5-ml aliquot was removed, diluted with an equal volume of saturated sodium bicarbonate solution, and extracted with 20 ml of dichloromethane. The dichloromethane solution was evaporated and the residue taken into 1 ml of 5×10^{-3} *M* biphenyl in dichloromethane as an internal standard. This solution was analyzed by gas chromatography on a 6-ft glass column containing 5% SE-30 on 80–100 mesh ANAKROM ABS at 160°. DNXB's, TNB, and biphenyl were easily separated and the concentrations determined by comparing the peak areas with those obtained from solutions of known concentrations of DNXB and TNB with the internal standard.

Determination of k_4 and k_5. The production of DNP was followed at 400 nm. All of the DNXB's and TNB showed pseudo-first-order kinetics with solutions of 0.2 *M* NaOH in 40% acetonitrile–60% water, where $\log (A_\infty - A_t)$ was plotted against time. At pH 7 the formation of DNP was extremely slow.

Determination of k_3. The O attack of nitrite on TNB to produce DNP was followed spectrophotometrically at pH 7 in 40% acetonitrile–60% water. Although N attack probably does occur, this would simply regenerate TNB.

Determination of k_1. Rate constant k_1 is a measure of the O attack of nitrite on DNXB. The production of DNP at pH 7 is expressed by

$$d[DNP]/dt = k_1[NO_2^-][DNXB] + k_3[NO_2^-][TNB] \quad (6)$$

It can be seen that initially the concentration of TNB is very small and the reaction expressed by eq 3 contributes little to the production of DNP. As the reaction progresses, the reaction shown by eq 3 may con-

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[6] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

[7] G. C. Hopkins, J. P. Jonak, H. J. Minnemeyer, and H. Tieckelman, *J. Org. Chem.*, **32**, 4040 (1967).

[8] J. I. G. Cadogan and D. T. Eastlick, *J. Chem. Soc. B*, 1314 (1970).

[9] M. Ringeissen, *C. R. Acad. Sci.*, **198**, 2180 (1934).

[10] N. Dokunikhin, Z. Moiseeva, and V. Mayatnikova, *Zh. Vses. Khim. Obshchest.*, **13** (4), 470 (1968); *Chem. Abstr.*, **70**, 12632r (1969).

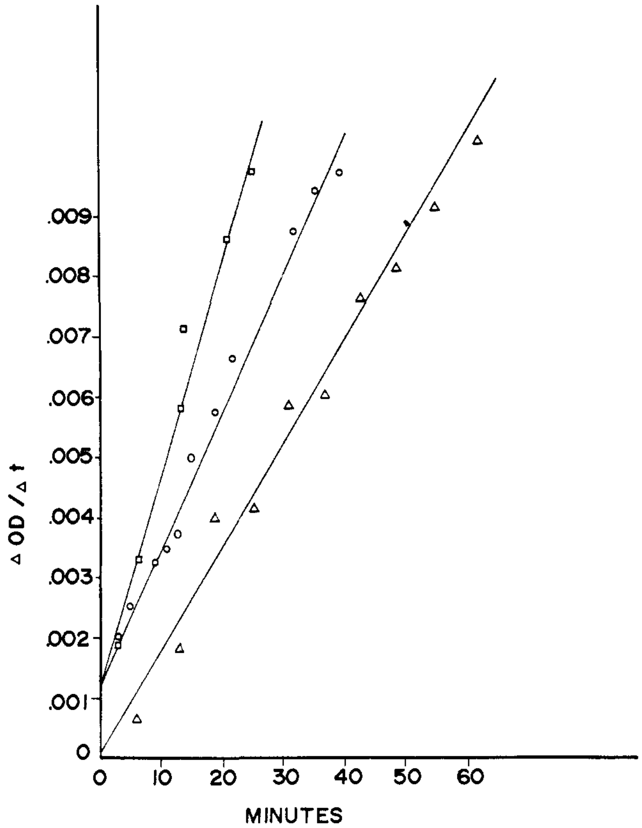

Figure 1. Least-squares plots of $\Delta_{OD}/\Delta t$ *vs.* t where the formation of DNP is being monitored. The reaction is DNXB + $NO_2^- \rightarrow$ DNP: DNClB (○), DNBrB (□), DNIB (△). At the intercept d[DNP]/dt = k_1[NO_2^-][DNXB].

tribute to a greater extent, resulting in an increase in d[DNP]/dt. The rate constant k_1 is determined by plotting the rate of change in optical density over short time intervals, ΔOD/Δt, *vs.* t, where t is the midpoint of Δt. The linear plot is extrapolated to $t = 0$, the intercept for ΔOD/Δt being found and converted to the initial value of d[DNP]/dt. Figure 1 shows these plots for DNXB, where X = Cl, Br, and I. The DNFB reaction shows no acceleration, indicating that in this case the reaction sequence corresponding to eq 2 and 3 is insignificant. The reactions of both DNClB and 2,4-dinitrobromobenzene (DNBrB) with nitrite ion give definite positive intercepts, whereas the plot for the 2,4-dinitroiodobenzene (DNIB) reaction has an intercept near zero, so that the reaction corresponding to eq 1 must not be important for DNIB. (The DNIB–nitrite reaction exhibited a period of induction during which no DNP appeared to be produced.) Values for k_1 were obtained by treating the data by the method of least squares.[11] Formation of DNP through the reaction of hydroxide ion with DNXB was also considered. It was calculated that during the first hour this path, reaction 5, contributes no more than one part in 5 × 10^4 of the DNP produced and therefore does not interfere with the calculation of k_1.

Determination of k_2 by Steady-State Approximation. The value of k_2 could be estimated by the steady-state approximation

$$\mathrm{d[TNB]/d}t = 0 = k_2[\mathrm{NO_2^-}][\mathrm{DNXB}] - k_3[\mathrm{NO_2^-}][\mathrm{TNB}] - k_4[\mathrm{OH^-}][\mathrm{TNB}] \quad (7)$$

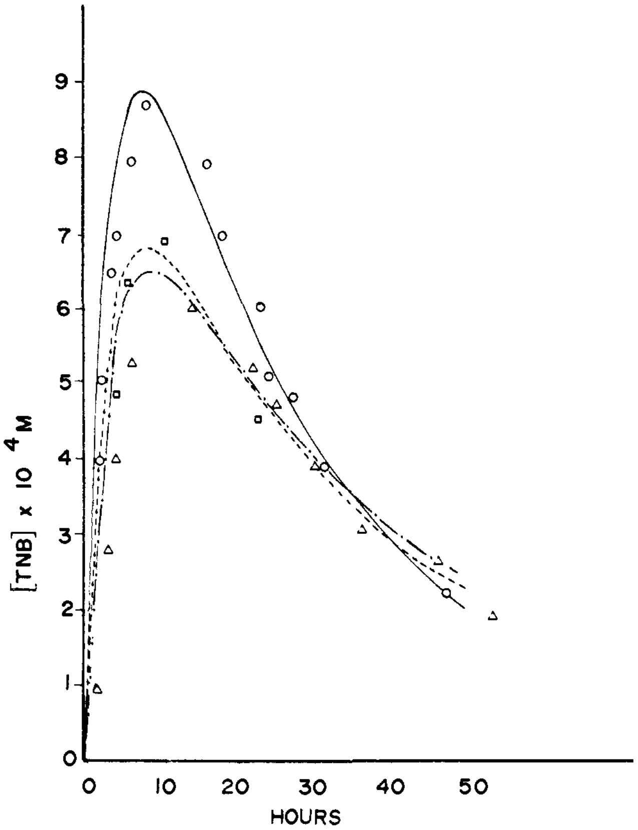

Figure 2. The points show the change in [TNB] measured by gas chromatography for the nitrite reaction with DNClB (○), DNBrB (□), and DNIB (△). The lines represent the computer fit of the data using eq 11 for DNClB (——), where $k_3 = 1.35 \times 10^{-2}$ and $k_2 = 1.60 \times 10^{-3}$; DNBrB (- - -), where $k_3 = 1.40 \times 10^{-2}$ and $k_2 = 1.20 \times 10^{-3}$; and DNIB (-·-), where $k_3 = 1.35 \times 10^{-2}$ and $k_2 = 1.10 \times 10^{-3}$.

Since the term k_4[OH^-] is very small at pH 7, the final relationship at steady state is

$$k_2 = k_3[\mathrm{TNB}]/[\mathrm{DNXB}] \quad (8)$$

The independently established value of k_3 was used and the concentrations of both TNB and the DNXB were determined by gas chromatography throughout the reaction. The point at which steady state was achieved was found from a plot of [TNB] *vs.* t. Figure 2 shows these plots.

Determination of k_2 at Non-Steady-State Conditions. Starting with the equation

$$\mathrm{d[TNB]/d}t = k_2[\mathrm{DNXB}][\mathrm{NO_2^-}] - k_3[\mathrm{TNB}][\mathrm{NO_2^-}] \quad (9)$$

the expression for k_2 at any time is

$$k_2 = k_3\frac{[\mathrm{TNB}]}{[\mathrm{DNXB}]} + \frac{\mathrm{d[TNB]/d}t}{[\mathrm{DNXB}][\mathrm{NO_2^-}]} \quad (10)$$

By determining the slope d[TNB]/dt from the curve at any time, t, and substituting into the above equation, the value of k_2 could be found. Values of k_2 for the DNClB and DNIB reactions were calculated from 12 data points for each reaction; k_2 for DNBrB was determined from only 4 data points.

Determination of k_2 by Treatment as a Consecutive Pseudo-First-Order Reaction. The reactions with

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[11] F. Daniels, J. Matthews, and J. Williams, "Experimental Physical Chemistry," 4th ed, McGraw-Hill, New York, N. Y., 1949, p 370.

Table I. Rate Constants (M^{-1} min^{-1}) for Reactions of 2,4-Dinitrohalobenzenes and 1,2,4-Trinitrobenzene with Nitrite and Hydroxide Ions in Aqueous Acetonitrile (3:2) at 25°

Dinitro-halobenzenes	k_1	k_5	$k_2{}^a$ (steady state)	$k_2{}^b$ (nonsteady state)	$k_2{}^c$ (data match)
Fluoro	4.0×10^{-2}	22	0	0	0
Chloro	9.7×10^{-8}	1.45×10^{-2}	1.98×10^{-3}	1.85×10^{-3}	1.60×10^{-3}
Bromo	8.7×10^{-8}	8.7×10^{-3}	2.23×10^{-3}	1.69×10^{-3}	1.20×10^{-3}
Iodo	Negligible	3.8×10^{-3}	1.24×10^{-3}	1.11×10^{-3}	1.10×10^{-3}

$k_3 = 1.50 \times 10^{-2}$; $k_4 = 68$

[a] k_2 determined by steady-state approximation. [b] k_2 determined by non-steady-state equation, reported as the average. The average deviations are as follows: chloro, 0.29×10^{-3}; bromo, 0.44×10^{-3}; iodo, 0.14×10^{-3}. [c] k_2 determined by matching theoretical curves to data. The values of k_3 were 1.35×10^{-2} for the chloro and iodo reactions and 1.40×10^{-2} for the bromo reaction.

which we are dealing are classic consecutive pseudo-first-order reactions.[12]

$$\mathrm{DNXB} \xrightarrow[\mathrm{NO_2^-}]{k_2} \mathrm{TNB} \xrightarrow[\mathrm{NO_2^-}]{k_3} \mathrm{DNP}$$

The expression for [TNB] is

$$[\mathrm{TNB}] = \frac{[\mathrm{DNXB}]_0 k_2}{(k_2 - k_3)}\left(e^{-k_2 t[\mathrm{NO_2^-}]} - e^{-k_3 t[\mathrm{NO_2^-}]}\right) \quad (11)$$

With the aid of a computer, theoretical curves were calculated from varying values of k_2 and k_3; the value of $[\mathrm{NO_2^-}]$ was held constant. The data were compared with the theoretical curves to find the best fit. Figure 2 shows the data superimposed on the theoretical curves. Table I lists the rate constants k_1 through k_5 that were determined for the four DNXB's.

Discussion

The three methods used in the determination of k_2 show very good agreement, especially in the cases of DNIB and DNClB. In the determination of the theoretical curves, the best fits were found when k_3 was 1.35×10^{-2}, which is only a 10% deviation from the experimental value. The large variation in values of k_2 for the DNBrB system and the difficulty in fitting the data to a theoretical curve can be partly attributed to a lack of sufficient experimental data.

An understandable relationship is found between the relative rates of O attack and N attack of nitrite ion and the electronegativity of the halogen displaced. The most electronegative of the series, DNFB, shows only O attack, whereas the least electronegative, DNIB, undergoes only N attack. DNClB and DNBrB fall between these extremes and clearly demonstrate both modes of displacement. An explanation for this mechanistic change may be drawn from Pauling's electronegativity scale;[13] here, the C–I bond should be almost completely covalent. As the electronegativity of the halogen increases, the C–X bond becomes more polar, making the reaction site increasingly positive. The positive carbon atom attracts the more electronegative oxygen of the nitrite ion, thereby favoring O attack. The carbon atom of the much less polar C–I bond is influenced by the more nucleophilic nitrogen atom of the nitrite ion. This explanation is consistent with the findings of Kornblum on the interaction of silver nitrite with alkyl bromides and iodides.[3] In these cases the silver ion exerts a polarizing effect on the carbon–halogen bond, promoting greater O attack by nitrite. Our work clearly demonstrates a system that is very sensitive to the two modes of attack by the nitrite ion *even in the absence of silver ion.* The change in mechanism results only from the change in degree of polarization of the carbon–halogen bond.[14]

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(12) A. Frost and R. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 166.

(13) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, New York, N. Y., 1960, p 88.

(14) It was suggested by a referee that an alternative explanation may be used to interpret the change in relative importance of N attack and O attack. He postulated that O attack by nitrite is reversible, whereas N attack is irreversible and is followed by halide loss to give TNB. When the halide to be displaced is fluoride, the first step by O attack should be much less reversible since fluoride ion is a good leaving group. In the case of DNIB, a true equilibrium would be established since the iodide ion is a very poor leaving group. Although this may be a valid explanation, we found no way to demonstrate it experimentally.