Nitrogen Isotope Effects in the Decomposition of Diazonium Salts

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L. L. BROWN AND J. S. DRURY

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

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The nitrogen isotope effects produced upon fractionally decomposing C_6H_5NNCl, $C_6H_5NNBF_4$, m-$ClC_6H_4NNBF_4$, o-, m-, and p-$CH_3C_6H_4NNBF_4$ were measured as a function of temperature. Between 5° and 70°C the data are well represented by the least-squares equation, $\log(k^{14}/k^{15}) = 6.949/T - 0.002528$. The experimental results agree well with those predicted from spectroscopic data. The data are consistent with the model in which decomposition occurs through the rupture of a single C–N bond. The observed isotope effect is insensitive to the nature and position of substituents on the aromatic ring and to the anion of the salt. The difference in the activation energy for the decomposition of the ^{14}N- and ^{15}N-labeled diazonium salts is 32 cal mole$^{-1}\cdot$deg^{-1}.

DIAZONIUM salts[1] normally decompose in S_N1-type reactions with evolution of nitrogen and formation of carbonium ions as indicated in (1):

$$ArN_2^+ \rightarrow Ar^+ + N_2. \qquad (1)$$

The decomposition of aliphatic diazonium salts is too rapid for study by conventional techniques, but aromatic salts are quite suitable for kinetic studies. Accordingly, we have used salts of the latter type to study the fractionation of nitrogen isotopes which occurs upon rupture of the C–N bond during the course of Reaction (1). It was of interest to study compounds which differed appreciably in their rates of reaction; consequently, we chose salts having rates of decomposition as fast or as slow as our experimental technique could accommodate. The salts having fast kinetics were then studied at a lower temperature, and those with slow kinetics at a higher temperature.

The experimentally observed results were compared with those expected theoretically. Spectroscopic data required in the latter calculations were obtained from infrared studies of normal and ^{15}N-substituted salts and from the literature.

The structure of benzene diazonium chloride has been studied by Romming.[2] He shows that the crystals are ionic, that the C–N–N chain is linear, and that N–N–C(1)–C(4) atoms are axial. This information indicates Structure I with nonequivalent N atoms

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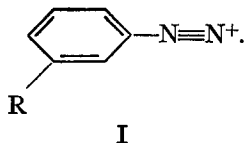
In later work, Lewis and Insole[3] measured k^{14} and

k^{15} independently and reported the value $k^{14}/k^{15} = 1.019 \pm 0.004$ for Reaction (1) at 49°C, using p-$CH_3C_6H_5NNBF_4$.

Saunders[4] calculated isotope effects from model structures of C–N and $(CH_3)_4N^+$ and predicted k^{14}/k^{15} values of 1.0432 and 1.0414 (59°C) for the respective models.

EXPERIMENTAL

Materials

Reagent-grade aniline, *ortho-* *meta-*, and *para*-toluidine, and *meta*-chloroaniline were diazotized and isolated as the fluoborate, as described by Roe.[5] The chloride salt was prepared for reaction without isolation. Several of the solid salts were stored at −78°C for six months without visible deterioration.

The $C_6H_5^{15}N^{14}NBF_4$ used in the spectral work was prepared from benzoyl chloride, $^{15}NH_4Cl$, and $Na^{14}NO_2$ according to Swan and Kelly.[6] A similar preparation containing normal abundance nitrogen in both positions was made for spectral comparison. The $^{15}NH_4Cl$ was prepared from 98.3% pure $H^{15}NO_3$ obtained from the Oak Ridge National Laboratory.

Equipment and Procedures

The various diazonium salts were decomposed in a cylindrical Pyrex reaction vessel which measured 3.5×27 cm. A single sidearm extending vertically to a stopcock allowed the tube to be evacuated prior to a run and allowed the product nitrogen to be recovered. The upper third of the reactor was a 50/40 T/S cap with a glass hook inside. A glass "bucket" containing a known quantity of solid salt was suspended over the frozen acid while the vessel was evacuated. When the reactor and contents had come to thermal equilibrium, the tube was inverted to bring the solid into solution at time zero. Estimates of the times for various frac-

[1] See, for broad coverage, the texts: K. H. Saunders, *The Aromatic Diazo Compounds* (Longmans, Green, and Company, Inc., New York, 1949); H. Zollinger, *Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds* (Interscience Publishers, Inc., New York, 1961).
[2] Chr. Romming, Acta. Chem. Scand. **17**, 1444 (1963).
[3] E. S. Lewis and J. M. Insole, J. Am. Chem. Soc. **86**, 34 (1964).

[4] W. J. Saunders, Jr., Chem. Ind. **1963**, 1661.
[5] *Organic Reactions*, edited by R. Adams (John Wiley & Sons, Inc., New York, 1949), Vol. 5, Chap. 4, Method II-A.
[6] G. A. Swan and P. Kelly, J. Chem. Soc. **1954**, 416.

tions of reaction were calculated from published rate constants. The reaction was quenched by freezing at liquid-nitrogen temperatures. The exact fraction of reaction was obtained from the amount of nitrogen recovered. The nitrogen was retained for isotopic analysis.

Reaction temperatures were controlled by means of a water bath; they are considered to have a maximum uncertainty of about $\pm 0.1°C$ because of the disturbing effect of removing the vessel from the bath to dissolve the solid. Dissolution of the solid usually required about 10 sec.

Isotopic samples were assayed as N_2 with a 6-in. radius, $60°$ sector, ratio mass spectrometer. The results were obtained directly in the form

$$r_{ms} = \frac{(^{29}N_2/^{28}N_2) \text{ gas}}{(^{29}N_2/^{28}N_2) \text{ total}}$$

$$= \frac{(^{15}N/^{14}N) \text{ gas}}{(^{15}N/^{14}N) \text{ total}}, \qquad (2)$$

where "gas" refers to nitrogen from the partially decomposed salt and "total" indicates nitrogen from a sample of completely decomposed salt. Since one of the nitrogen atoms of the decomposed diazonium salt was isotopically inert in the significant bond-breaking process, the isotopic ratio given by (2) was corrected according to the relationship

$$r = r_{ms}(1+p) - p, \qquad (3)$$

where p accounts for the isotopic differences in synthesizing reagents and equals

$$\frac{(^{15}N/^{14}N)_{NO_2^-}}{(^{15}N/^{14}N)_{amine}}.$$

Equation (3) includes the approximation

$$\frac{(^{14}N)_{NO_2^-}}{(^{14}N)_{amine}} = 1.000$$

for normal abundance nitrogen. Since p never exceeded 1.009, the simplified form

$$r = 2r_{ms} - 1 \qquad (4)$$

was used. In both (3) and (4) the meanings of r and r_{ms} are as in Eq. (2).

The infrared studies were made with mineral oil mulls between KBr disks on a Perkin–Elmer Model 521 spectrometer. The spectra of normal and ^{15}N-substituted salts were scanned routinely from 4000 to 350 cm^{-1}. Regions where isotope shifts were observed were re-examined in detail.

RESULTS AND DISCUSSION

The ratios of specific rate constants for the separate ^{14}N and ^{15}N reactions were computed by

$$k^{14}/k^{15} = \log(1-f)/\log(1-rf), \qquad (5)$$

TABLE I. Kinetic isotope-effect data for diazonium salts at 40.5°C.

Salt	f [a]	r [a]	k^{14}/k^{15} [a]
C_6H_5NNCl	0.0408	0.9581	1.045
	0.0873	0.9579	1.046
	0.181	0.9603	1.045
	0.291	0.9650	1.042
		Av.	1.044±0.003
$C_6H_5NNBF_4$	0.0928	0.9612	1.042
	0.127	0.9599	1.045
	0.135	0.9646	1.039
	0.196	0.9606	1.046
		Av.	1.043±0.005
o-$CH_3C_6H_4NNBF_4$	0.116	0.9579	1.047
	0.147	0.9600	1.045
	0.183	0.9614	1.045
	0.214	0.9616	1.045
		Av.	1.045±0.001
m-$CH_3C_6H_4NNBF_4$	0.0958	0.9574	1.047
	0.0984	0.9575	1.047
	0.126	0.9578	1.047
	0.194	0.9590	1.048
		Av.	1.047±0.001
p-$CH_3C_6H_4NNBF_4$	0.0474	0.9567	1.046
	0.0971	0.9578	1.046
	0.146	0.9587	1.048
	0.199	0.9599	1.047
		Av.	1.047±0.001
m-$ClC_6H_4NNBF_4$	0.0630	0.9792	1.045
	0.121	0.9800	1.044
	0.172	0.9812	1.043
	0.205	0.9815	1.043
		Av.	1.044±0.001
Average for all salts at 40.5°C			1.045

[a] See text for definitions, Eq. (5).

where f is the fraction of the reaction completed, and r is as defined above.

Results of kinetic studies performed at $40°$ are given in Table I. Data for studies at $6.9°$ and $68.5°$ are presented in Table II. It may be seen from these data that the kinetic isotope effect is temperature dependent, but, within the limits of experimental error, it is sensitive neither to the nature nor position of substituents on the aromatic ring, nor to the anion of the salt. Accordingly, estimates of the isotope effect were obtained by averaging all data obtained at a given temperature.

The frequencies and assignments of vibrational modes pertinent to the decomposition of the normal and ^{15}N-substituted salts are listed in Table III. (Lines due to C_6H_5 and BF_4 structures are omitted.) Four fundamental vibrations were expected: the two C–N–N bends, the N–N stretch, and the C–N stretch. Sharp

TABLE II. Kinetic isotope-effect data for diazonium salts at 6.9° and 68.5°C.

Temp. (°C)	Salt	f^a	r^a	k^{14}/k^{15} ^{a}
6.9	m-$CH_3C_6H_4NNBF_4$	0.0521	0.9515	1.053
		0.105	0.9517	1.054
		0.156	0.9520	1.052
		0.162	0.9542	1.053
			Av.	1.053±0.001
	o-$CH_3C_6H_4NNBF_4$	0.0611	0.9519	1.052
		0.0935	0.9520	1.053
		0.193	0.9529	1.055
		0.242	0.9560	1.053
			Av.	1.053±0.002
	Average for all salts at 6.9°C			1.053
68.5	p-$CH_3C_6H_4NNBF_4$	0.0579	0.9600	1.043
		0.0604	0.9633	(1.039)
		0.113	0.9618	1.042
		0.114	0.9613	1.043
		0.137	0.9612	1.043
			Av.	1.043±0.001
	m-$ClC_6H_4NNBF_4$	0.0640	0.9593	1.044
		0.0992	0.9586	1.045
		0.153	0.9637	1.041
		0.213	0.9655	1.040
			Av.	1.043±0.004
	Average for all salts at 68.5°C			1.043

^{a} See text for definitions, Eq. (5).

bands associated with the first three of these vibrations were observed with a precision of ±2 cm^{-1}. However, a wide absorption band almost completely obscured the spectrum between 1000 and 1200 cm^{-1}, the region in which the C–N stretch was expected, and no satisfactory estimate of the frequency of this vibration could be obtained. A broad, intermediate strength

TABLE III. Isotope shifts in the spectra of ^{15}N-substituted benzene diazoniumfluoborate.

Band	Frequency (cm^{-1})		Assignment
	$C_6H_5^{14}NNBF_4$	$C_6H_5^{15}NNBF_4$	
I	455	451	C–N–N bend
II	533	526	C–N–N bend
III	910	902	$2(I)$
IV	2296	2251	N≡N stretch
V	620	618	
VI	1222	1218	
VII	3368	3324	

band (VII, Table III) was observed near 3350 cm^{-1} which may represent the sum of the C–N and N–N stretching frequencies, but its assignment and center were in sufficient doubt to preclude its use in computing an isotope effect. Rather, we chose the alternate course to be described later. Listed in Table III are two additional weak, unassigned absorption lines not previously reported for a ^{15}N-substituted diazonium salt.

The prediction of isotopic rate constant ratios from spectroscopic data is discussed by Melander[7] and by Bigeleisen and Wolfsberg.[8] The latter authors show that, for appropriate reactions, the ratio of reaction rate constants may be estimated by Eq. (6),

$$\frac{k_1}{k_2}\frac{s_2 s_1^\dagger}{s_1 s_2^\dagger} = \left(\frac{\nu_{1L}^\dagger}{\nu_{2L}^\dagger}\right)\left[1 + \frac{\bar{\gamma}}{24}\left(\frac{\hbar c}{kT}\right)^2 \sum_i^{3n}\left(\frac{1}{m_{1i}} - \frac{1}{m_{2i}}\right)(a_{ii} - a_{ii}^\dagger)\right],$$

(6)

where the subscripts 1 and 2 refer to the light and heavy isotopic species, respectively, the superscript † refers

TABLE IV. Predicted and observed isotope effect for decomposition of diazo salts.

	6.8°C	40.5°C	68.5°C
Predicted			
TIF	1.015$_7$	1.015$_7$	1.015$_7$
TDF	1.035$_0$	1.027$_7$	1.023$_3$
k^{14}/k^{15}	1.051	1.044	1.039
Experimental			
k^{14}/k^{15}	1.053	1.045	1.043

to the activated complex, s is the symmetry number of the molecule, $\nu_{1L}^\dagger$ and $\nu_{2L}^\dagger$ are the imaginary frequencies of the activated complexes along the reaction coordinates, m is the mass of the participating isotope, a_{ii} is the force constant characteristic of the ruptured bond, and $\bar{\gamma}$ is a frequency-dependent correction factor; the other symbols have their usual significance. In using (6) to estimate the ratio k^{14}/k^{15} for the decomposition of diazonium salts, the temperature-independent factor (TIF) $\nu_{1L}^\dagger/\nu_{2L}^\dagger$ was estimated on the basis of the simple two-atom model[9] as $[(\frac{1}{12} + \frac{1}{14})/(\frac{1}{12} + \frac{1}{15})]^\frac{1}{2} = 1.0157$. In computing the predicted temperature-dependent factor, the force constant a_{ii} was taken as 7.5 dyn cm^{-1}, a value recently determined by Mushkin et al.,[10] for the similar, though not identical, C–N bond in cyanamide. The value of $\bar{\gamma}$ was taken as 0.73 for a midrange temperature of 312°K and 1100 cm^{-1}, a

[7] L. Melander, *Isotope Effects on Reaction Rates* (The Ronald Press Company, New York, 1960). See especially Chap. II.
[8] J. Bigeleisen and M. Wolfsberg, Advan. Chem. Phys. 1, 15 (1958).
[9] Other models by which the temperature-independent factor may be estimated, such as the two-fragments case, are discussed in Refs. 7 and 8.
[10] Yu. I. Mushkin and A. I. Finkelshtein, Opt. i Spektroskopiya 13, 289 (1962).

typical frequency[11] for this vibration in related molecules.

The predicted and experimentally determined rate-constant ratios for the decomposition of ^{14}N- and ^{15}N-substituted diazonium salts are listed in Table IV. Agreement between the two sets of data is good; the data are thus consistent with our premise that the thermal decomposition of diazo salts is adequately described by rupture of a single C–N bond.

Our rate-constant ratios, both experimental and computed, exceed that reported by Lewis and Insole[3] by more than the reported limits of error. We believe the lack of accord is due to the use, by the latter workers,

of the more difficult absolute, noncompetitive method of measuring rate constants, and by the fact that they made only one determination.

Our kinetic data may be expressed by the least-squares equation,

$$\log(k^{14}/k^{15}) = 6.949/T - 0.002528. \qquad (7)$$

Equation (7) yields an estimate of E, the difference in activation energy for the decomposition of the ^{14}N- and ^{15}N-labeled diazonium salts of 32 cal mole$^{-1}\cdot$deg^{-1}.

ACKNOWLEDGMENTS

[11] (a) See Ref. 10 in text; (b) C. B. Moore and G. C. Pimentel, J. Chem. Phys. **40**, 329–342 (1964); (c) R. J. LeFerve, M. F. O'Dwyer, and R. L. Werner, Australian J. Chem. **6**, 341 (1953).

Exchange and Relativistic Effects on Pi Bonding in the Uranyl Ion*

JOHN B. NEWMAN

Carlyle Barton Laboratory, The Johns Hopkins University, Baltimore, Maryland

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Overlap integrals for the uranyl ion were calculated using Hartree–Fock–Slater and Hartree relativistic U^{5+} 5f and 6d wavefunctions. Earlier primary overlap calculations by Belford and Belford, using solutions which are approximately Hartree functions, gave π larger than σ overlaps. Exchange effects tend to equalize the σ and π overlaps, and a case was found where the σ overlaps exceed the π values. The relativistic effects are indirect and more pronounced for the 5f orbital. They tend to equalize the σd and πf overlaps, and to increase the πd value which nevertheless remains the largest. These results are indicative of a uranyl structure having strong πd, and weak σf primary bonds, and having at most weak 5f orbital involvement in the secondary bonding. Thus, the overlap results obtained using exchange and relativistically corrected uranium wavefunctions support the view of uranyl complex structures as proposed by Belford and Belford and by Coulson and Lester.

THE chemical, magnetic, and spectroscopic properties of the uranyl ion have been studied extensively.[1] Progress has been slow toward obtaining an adequate theory of the uranyl behavior, not only because of the many complexities involved but also because of the lack of uranium wavefunctions. Assuming predominantly sigma bonding, Eisenstein and Pryce[2] have given a theory of the uranyl electronic structure. On taking molecular orbitals filled in the order of the overlap values (estimated from Slater-type oribtals), McGlynn and Smith[3] have proposed an electronic configuration for the uranyl ground state. In the first numerical evaluation of the primary uranyl

overlaps, Belford and Belford[4] found pi bonding to be important, and the maximum overlap criterion for these results leads to a different uranyl ground-state configuration from the one given by McGlynn and Smith. Calculations of the primary-bond overlaps were made using solutions of the radial wave equations which Belford and Belford computed numerically with a potential gotten from the Hartree U^{6+} core solution. Pi bonding has been proposed by Hanauer, Dabbs, Roberts, and Parker[5] to account for the sign of quadrupole coupling constant observed for paramagnetic actinyl ions. Values of the overlaps between uranyl and its ligands, i.e., for secondary bonding, have been found by Coulson and Lester[6] using Slater-type orbitals for uranium and hydrogen 1s orbital for the ligands.

Here we give new values of the primary-bonding uranyl overlap integrals found with U^{5+} 5f and 6d

[1] E. Rabinowitch and R. L. Belford *Spectroscopy and Photochemistry of Uranyl Compounds* (The Macmillian Company, New York, 1964).

[2] J. C. Eisenstein and M. H. L. Pryce, Proc. Roy. Soc. (London) **A229**, 20 (1955).

[3] S. P. McGlynn and J. M. Smith, J. Mol. Spectry. **6**, 188 (1961).

[4] R. L. Belford and G. Belford, J. Chem. Phys. **34**, 1330 (1961).

[5] S. H. Hanauer, J. W. T. Dabbs, L. D. Roberts, and G. C. Parker, Phys. Rev. **124**, 1512 (1961).

[6] C. A. Coulson and G. R. Lester, J. Chem. Soc. **1956**, 3650.