

This 3c-4e bond appears to occur rather frequently when a less electronegative atom forms bonds with halogens and where the usual closed shell compounds result in a low coordination number for the less electronegative atom, e.g., PF_3 , SCL_2 , Cl-F etc. The coordination number can be increased and some further bonding achieved by forming 3c-4e bonds without expanding the valence shell, e.g., PF_6 , SCL_4 and SF_6 , ClF_5 , etc.⁹ It now appears that Xe is the final, less electronegative member of such a sequence.

Using Mulliken's method¹⁰ rough values of the electronegativities of the rare gases can be obtained, assuming that the electron affinity of the rare gases is negligible, by using their known ionization constants.⁷ The results are

Element	He	Ne	Ar	Kr	Xe	Rn
Electronegativity	4.5	4.0	2.9	2.6	2.25	2.0

However rough these values may be, the electronegativity of Xe must be considerably less than that of F, fulfilling the requirements of this proposal. Clearly this proposal allows for XeF_4 and XeF_6 by using the two other 5p-orbitals of Xe to form 3c-4e bonds. But since each bond removes some charge from Xe, the high ionization energy of Xe must destabilize the higher coordination numbers. Steric repulsions may also be a factor. (Because of the negative charge carried by F coulombic warping of planar XeF_4 cannot be excluded.)

One may compare XeF_4 with IF_5 to learn something of the stability of XeF_4 . ΔH° and ΔH° for formation of IF_5 are -180.6 and -202.6 kcal./mole.⁸ IF_5 is essentially a square planar molecule with a shorter I-F bond normal to the IF_5 plane.⁸ Correlation diagrams and MOs for the two are shown in Fig. 2. It is to be noted that IF_5 and XeF_4 are stabilized by three and two bonding pairs, respectively, the extra pair providing for the shorter, out of plane, I-F bond. ΔH° and ΔG° for XeF_4 might then be about two-thirds of that for IF_5 if all else were equal. But the bonding removes charge from the central atom, further destabilizing XeF_4 relative to IF_5 since the first ionization energy of Xe exceeds that of I by 38.6 kcal./mole.⁷ Hence ΔH° and ΔG° may be more than 100 kcal./mole greater for XeF_4 (possibly much greater if considerable electron density is removed from the central atom), but even this leaves a surprising stability for XeF_4 . Indeed, since ΔH° and ΔG° for BrF_5 are -127.9 and -101.9 kcal./mole,⁸ the prospects for KrF_4 may not be altogether bleak.

Though distances are not known for IF_5 , 3c-4e I-F distances of 2.00 Å. have been found for IO_2F_2^- .¹¹ By extrapolation the radius of Xe should be about 0.04 Å. less than that I, suggesting an Xe-F distance of about 1.96 Å.

Finally, from this proposal it is to be expected that oxyfluorides of Xe^2 will contain pairs of linear F-Xe-F 3c-4e bonds, and that similar bonding may help stabilize XePtF_6 .¹²

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SPECTROSCOPIC AND CHEMICAL EVIDENCE FOR THE NO_3 FREE RADICAL IN SOLUTION AT ROOM TEMPERATURE

Sir:

A great deal of spectroscopic and kinetic evidence now is available to show that the short-lived NO_3 radical can be produced in the gas phase by either the decomposition or the chemical oxidation of the lower nitrogen oxides. Earlier outstanding papers on this subject are the detailed kinetic work by Ogg¹ and Johnston² in elucidating the mechanism of the famous N_2O_5 decomposition reaction and the investigation by Jones and Wulf³ which summarizes the prior chemical and spectroscopic data for NO_3 in the gas phase. Each of these earlier studies has been well corroborated and extended now by the excellent work of Davidson and co-workers^{4,5} who have successfully generated the NO_3 radical in gas phase or in a low temperature matrix by either shock wave, photolysis, chemical oxidation, or electrical discharge techniques.

In contrast to previous studies and in accord with an earlier suggestion by Uri,⁶ we have succeeded in generating the NO_3 radical by the photolysis of ceric ammonium nitrate solutions with light quanta in the 280-400 m μ range. This represents not only a new chemical way to generate the NO_3 radical but also an easy method to introduce it homogeneously into solution at a controlled rate.

Direct spectroscopic evidence that the NO_3 radical is generated in solution by our new method was obtained by the flash photolysis technique. The principal NO_3 absorption bands observed after a 100-joule photolysis flash into a 10-cm. cell filled with an aqueous solution containing 1.6×10^{-4} M ceric ammonium nitrate and 5.9 M nitric acid at room temperature are presented in Fig. 1. These data represent the optical

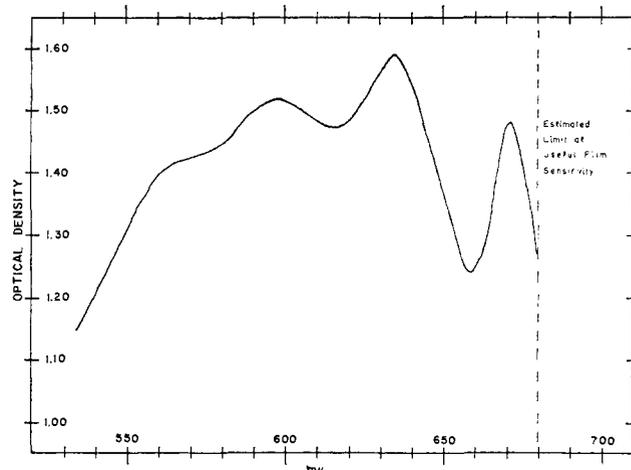


Fig. 1.—Flash absorption spectrum of the NO_3 radical in solution at room temperature.

density of the NO_3 in this solution and were obtained by taking the differences in transmission between two exposures on the same Kodak 103-F film strip measured on a microdensitometer. The background spectrum was exposed just prior to, and the NO_3 spectrum was taken about 85 microseconds after, the photolysis flash using a grating spectrograph with a linear dispersion of 15 Å./mm. No other component or possible intermediate in the solution except NO_3 gives such an absorption spectrum. Although the bands of the NO_3 solution

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spectrum are broader than the gas phase spectrum by a factor of two or three as expected, they are in excellent agreement with the results of DeMore and Davidson⁵ in frozen matrix. This solution spectrum based on our assignments for the maxima of the two most prominent bands at 635 and 671 $m\mu$, shows only a slight solvent shift of about 10 $m\mu$ when compared with the 623 and 663 $m\mu$ band heads measured by Ramsay⁷ for the gas phase spectrum.

The estimated lifetime of the NO_3 radical is approximately 200 microseconds maximum in the aqueous nitric acid system. However, its apparent lifetime is noticeably shortened upon the addition of acetic acid to the medium. This decrease in NO_3 lifetime was shown to be related to the amounts of acetic acid added as were the yields of carbon dioxide and methane isolated from these photolyzed solutions. When the added acetic acid concentration is about 1.0 M , we are just barely able to detect the NO_3 radical with our present apparatus. A more accurate and comprehensive study of the NO_3 lifetime and its dependence on various solution parameters is now in progress.

Our method of forming the NO_3 radical makes it feasible to study its specific reactivity and to evaluate its possible synthetic uses as a new reagent for the nitration and oxidation of a given substrate. Further, we believe that such applications provide additional chemical evidence that the NO_3 radical is the probable reaction initiator in a variety of solvent systems. For example, we find that the photolysis of a solution containing 0.02 M ceric ammonium nitrate in glacial acetic acid gives rise to products whose yields as a function of temperature and light intensity are best explained by secondary radical displacement processes initiated by NO_3 radical formed in the primary photochemical step. The chemical data given here support this contention. The ceric salt is always reduced with the loss of one nitrate group from the original ion complex. The acetic acid is decomposed at high flash intensities to yield only carbon dioxide and methyl nitrate as the major observable products, with minor yields of methane, methanol, and methyl acetate. The decreased quantum yield of methane with increasing light intensities and the marked temperature independence of the methane yield definitely preclude the possibility that methyl radicals (derived, for instance, by the decomposition of prior acetoxy radicals) are a probable source of the methyl nitrate product in this system. The quantum yield for cerium reduction is found to be 0.36 at 30°, which shows the initiating reaction to be remarkably efficient and unusual when compared to other reported photoreductions of cerium.

On the basis of both the spectroscopic and chemical evidence cited and also because we have shown by spectrophotometric and electrophoresis studies that the most probable photoreactive ceric species necessary to generate the NO_3 radical are the $\text{Ce}(\text{NO}_3)_4$ molecule and the hexanitratocerate ion, $\text{Ce}(\text{NO}_3)_6^{--}$, we believe that the primary photochemical process most consistent with all the data in the systems we have studied can be represented as



whereby the absorbed quantum initiates an intramolecular oxidation-reduction reaction in the excited state of the absorbing species by means of an electron charge exchange between one of the closely coupled nitrate ions and its associated cerium(IV) atom. This action results in the formation of a cerium(III) species and the efficient release of a very reactive NO_3 radical which can then attack other components in the solution. The details of this specific attack on glacial acetic acid

and our interpretation of the ensuing reaction mechanism will be the subject of a subsequent publication.

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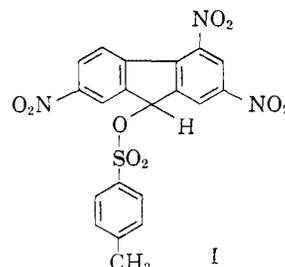
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ENHANCEMENT OF ACETOLYSIS RATES BY CHARGE-TRANSFER COMPLEXING¹

Sir:

We wish to report evidence that the reactivity of suitably constituted compounds can be strongly modified through charge-transfer complexing. Rates of acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfo-



nate (I)² at 100° are increased by addition of aromatic donors in 0.02 M concentration (Table I).

TABLE I
EFFECT OF AROMATIC DONORS IN THE ACETOLYSIS OF 2,4,7-TRINITRO-9-FLUORENYL *p*-TOLUENESULFONATE^a

Donor	Temp., ^b °C.	10 ² [Donor], M	10 ² k_1 , sec. ⁻¹
None	99.3	...	1.38 ± 0.04
None	99.9	...	1.86 ± 0.02
Hexamethylbenzene	99.3	2.02	2.08 ± 0.06
Hexamethylbenzene	99.9	1.86	2.50 ± 0.03
Hexaethylbenzene	99.9	1.85	1.79 ± 0.01
Phenanthrene	99.3	2.00	2.61 ± 0.13
Acenaphthene	99.3	2.01	7.05 ± 0.27
Anthracene	99.3	2.01	13.98 ± 1.07
Anthracene	99.9	0.200	3.18 to 2.61 ^c

^a Concentration of *p*-toluenesulfonate was 0.0020 M for all runs. ^b Temperatures were maintained at 99.3 ± 0.1° and 99.9 ± 0.02°. ^c Instantaneous first order rate constants showed a regular decrease over the range of the reaction studied (12 to 91%).

The results of a more detailed study involving phenanthrene-donor are summarized in Table II. Plots of

TABLE II
ACETOLYSIS OF 2,4,7-TRINITRO-9-FLUORENYL *p*-TOLUENESULFONATE IN THE PRESENCE OF PHENANTHRENE

Temperature					
55.85 ± 0.01°		85.0 ± 0.01°		99.9 ± 0.02°	
10 ² [Donor], M	10 ² k_1 , sec. ⁻¹	10 ² [Donor], M	10 ² k_1 , sec. ⁻¹	10 ² [Donor], M	10 ² k_1 , sec. ⁻¹
0	1.86 ± 0.03	0	4.44 ± 0.08	0	1.86 ± 0.02
0.971	2.56 ± 0.01	0.943	5.67 ± 0.06	0.931	2.36 ± 0.03
1.94	3.29 ± 0.09	1.89	7.04 ± 0.06	1.86	2.86 ± 0.02
3.89	4.99 ± 0.04	3.77	9.43 ± 0.12	3.72	3.61 ± 0.01
4.85	5.72 ± 0.09	5.66	11.57 ± 0.14	5.58	4.35 ± 0.03
5.82	6.33 ± 0.05				
6.79	7.05 ± 0.03				

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