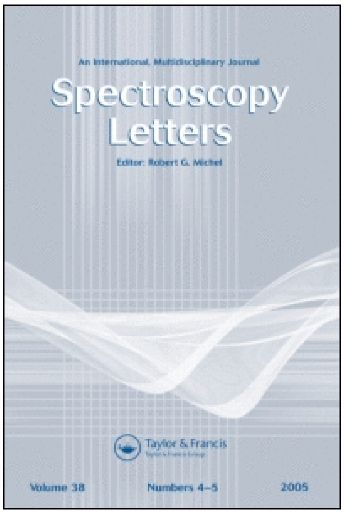

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SPECTROSCOPIC EVIDENCE FOR DONOR-INDUCED FORMATION OF NITROSONIUM IN ACIDIFIED SOLUTIONS OF ALKYL NITRITES

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SPECTROSCOPIC EVIDENCE FOR DONOR-INDUCED FORMATION OF NITROSONIUM IN ACIDIFIED SOLUTIONS OF ALKYL NITRITES

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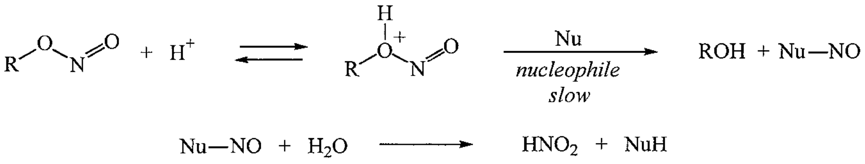
ABSTRACT

The "donor-induced" generation of nitrosonium cation in acidified solutions of alkyl nitrites in dichloromethane is demonstrated spectroscopically. Electron-rich organic molecules, including polymethylbenzenes and thioethers, affect the donor-induced release of nitrosonium as the corresponding electron donor–acceptor complex [donor, NO^+]. These complexes are spectrally identified using a combination of UV–vis and IR spectroscopy. The almost quantitative formation of the [donor, NO^+] EDA complex with hexamethylbenzene and butyl sulfide as donors is verified with UV–vis spectroscopy.

Key Words: Nitrosonium; Alkyl nitrites; UV–vis; IR

INTRODUCTION

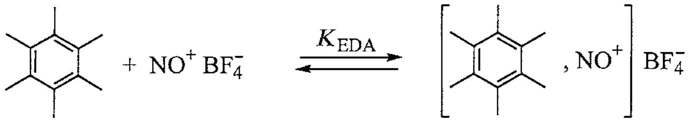
Alkyl nitrites are effective nitrosating agents in the presence of acid (1) and, furthermore, are proposed intermediates in the nitrosation of amines in the



Scheme 1.

presence of alcohols (2). Iglesias et al. (3) proposed that the acidic hydrolysis of alkyl nitrites followed a concerted mechanism. Thus, the low concentrations of protonated alkyl nitrite expected to be formed in solution react directly with a nucleophile to generate a more active nitrosating agent. Thus, in the presence of chloride the authors proposed that nitrosyl chloride was formed and subsequently hydrolyzed to nitrous acid as shown in Scheme 1 (Nu=Cl^-).

It has independently been demonstrated that nitrosonium forms strong electron donor–acceptor (EDA) complexes with a variety of electron-rich organic molecules. Most noteworthy among these is hexamethylbenzene that forms a strong EDA complex with nitrosonium salts as shown in Equation (1):



(1)

The formation constant for this complex is high with $K_{EDA} = 3 \times 10^4\ M^{-1}$ (4). Other electron-rich organics, including ethers, thioethers (5), and nitrosoarenes (6), also form EDA complexes with nitrosonium. In this communication we report our preliminary results describing the use of this strong EDA complexation to quantify the "donor-induced" generation of nitrosonium in acidified solutions of alkyl nitrites.

EXPERIMENTAL

Materials

Hexamethylbenzene, pentamethylbenzene, durene, 1-octanol, trifluoroacetic acid, and butyl sulfide (Aldrich) were used as received. Octyl nitrite was prepared from 1-octanol according to the procedure given in (7). Dichloromethane (Fisher) was distilled from calcium hydride and stored in a Schlenk flask, under an argon atmosphere.

UV–vis Characterization of Donor-Induced Generation of Nitrosonium

Hexamethylbenzene

A solution of hexamethylbenzene (5.2 mg, 1.6×10^{-3} *M*) and octyl nitrite (1.5 mg, 4.7×10^{-4} *M*) in dry dichloromethane (20 mL) was prepared in a Schlenk tube, under an argon atmosphere. 4 mL of this solution was transferred by syringe to a 1-cm cuvet fitted with a rubber septum and flushed with argon. The UV–vis absorption spectrum was measured and showed no significant absorption above 300 nm. Trifluoroacetic acid (1.8 mg, 4×10^{-3} *M*) was added with the aid of a microsyringe and the UV–vis absorption spectrum of the resultant pale pink solution immediately recorded (see Fig. 1). The spectrum was identical with an authentic UV–vis absorption spectrum of the hexamethylbenzene–nitrosonium EDA complex exhibiting two maxima at 335 and 510 nm. The absorbance at 335 nm was 1.32. Given the extinction coefficient of [HMB, NO^+] at 335 nm of 3100 mol^{-1} cm^{-1}, the concentration of the complex is calculated to be $1.32/3100 = 4.3 \times 10^{-4}$ *M*.

Butyl Sulfide

The same procedure was used with 0.0011 *M* butyl sulfide in place of hexamethylbenzene. Due to the low stability of the [sulfide, NO^+] complex, the

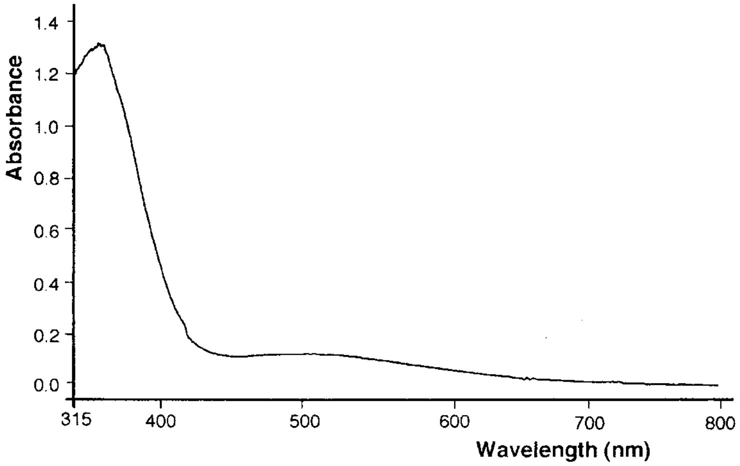


Figure 1. UV–vis absorption spectrum observed with a dichloromethane solution of octyl nitrite (4.7×10^{-4} *M*), trifluoroacetic acid (4×10^{-3} *M*), and hexamethylbenzene (1.6×10^{-3} *M*).

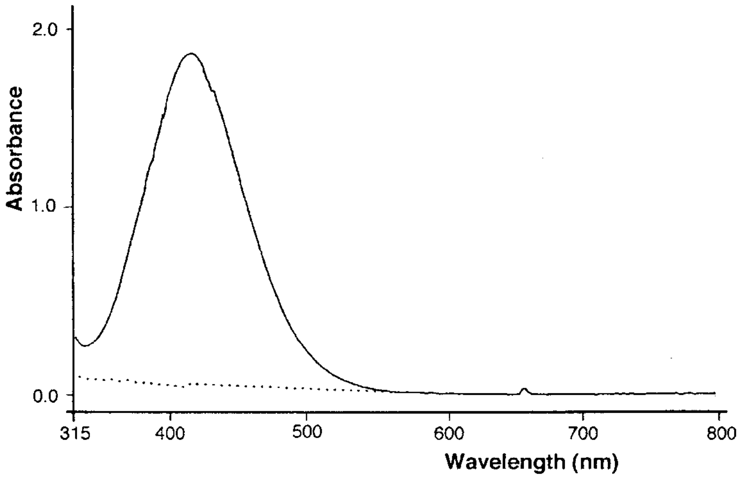


Figure 2. UV–vis absorption spectrum observed with a dichloromethane solution of octyl nitrite (4.7×10^{-4} *M*), trifluoroacetic acid (4×10^{-3} *M*), and butyl sulfide (1.1×10^{-3} *M*). The dotted line represents the absorption in the absence of butyl sulfide.

spectra were recorded at −78°C. A strong absorption centered at 400 nm was observed corresponding to the butyl sulfide–nitrosonium EDA complex. The absorption at $\lambda_{max} = 400$ nm of 1.8 corresponded to a [butyl sulfide, NO^+] complex concentration of 4.5×10^{-4} *M* (see Fig. 2).

IR Characterization of Donor-Induced Generation of Nitrosonium

Hexamethylbenzene

A 0.5 *M* solution of octyl nitrite in dichloromethane was prepared in a Schlenk tube, under an argon atmosphere, and transferred with the aid of a canulla to a CaF_2 cell fitted with rubber septa. The IR spectrum was recorded and the cell flushed with dichloromethane. There was no absorption in the region between 1500 and 2270 cm^{-1}. A separate dichloromethane solution containing 0.5 *M* octyl nitrite and 0.5 *M* trifluoroacetic acid was prepared in a Schlenk flask, under an argon atmosphere. The IR spectrum was recorded as before and there was no significant absorption in the range 1850–2270 cm^{-1}; the strong carbonyl absorption of the trifluoroacetic acid was visible at 1780 cm^{-1}. A 0.1 *M* solution of hexamethylbenzene in dichloromethane was prepared and the IR spectrum recorded, and there was no absorption in the range 1850–2270 cm^{-1}. Hexamethylbenzene (49.1 mg) was then added to 3 mL of the dichloromethane solution of octyl nitrite (0.5 *M*) and

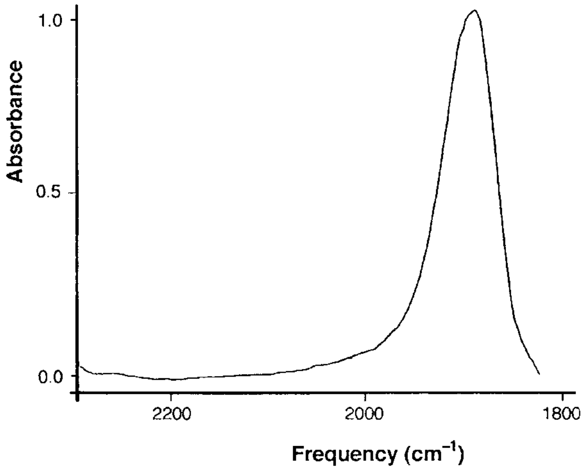


Figure 3. Difference IR spectrum of a dichloromethane solution containing pentamethylbenzene (0.5 *M*), octyl nitrite (0.5 *M*), and trifluoroacetic acid (0.5 *M*).

trifluoroacetic acid (0.5 *M*), under an argon atmosphere, and the mixture stirred vigorously for 5 min to dissolve the solid. The IR spectrum of the resultant dark red solution was recorded and a new absorption observed at 1860 cm^{-1}. Subtraction of the absorptions due to dichloromethane, octyl nitrite, trifluoroacetic acid, and hexamethylbenzene from this spectrum resulted in a single peak at 1859 cm^{-1}, as shown in Figure 3.

Pentamethylbenzene and Durene

IR spectral analysis was performed as described earlier; however, the concentration of the methylbenzene was adjusted. Thus, 0.5 *M* pentamethylbenzene and 1.0 *M* durene were used and the absorptions of polymethylbenzene complexed nitrosonium were observed at 1890 and 1910 cm^{-1}, respectively.

RESULTS AND DISCUSSION

Authentic nitrosonium complexes of various organic donors have previously been prepared from nitrosonium salts and spectrally characterized. In addition, selected X-ray structures have confirmed the composition of these complexes (4,6). UV–vis absorption spectroscopy has proven to be the method of choice for the rapid characterization of organic donor–nitrosonium complexes since the complexes are generally intensely colored. In this study, I used two donors that have high affinity to complex nitrosonium: hexamethylbenzene and butyl sulfide. The resultant nitrosonium EDA complexes formed are uniquely characteristic: the hexamethylbenzene–nitrosonium complex is red and exhibits two $\lambda_{\max}$ at 335 and 510 nm while the butyl sulfide–nitrosonium is bright yellow with $\lambda_{\max}$ at 400 nm. The absorption spectra shown in Figures 1 and 2 clearly demonstrate the formation of the corresponding nitrosonium EDA complex. Furthermore since the extinction coefficients of these complexes are known the absorption maxima observed can be used to calculate the concentration of each complex in the solution. Using this method our preliminary results indicate the quantitative formation of [donor, NO^+] complexes with both of these donors even at concentrations as low as 4×10^{-4} *M* octyl nitrite and 4×10^{-3} *M* trifluoroacetic acid and hexamethylbenzene or butyl sulfide. This is described in Equation (2):

$$\text{DONAR} + \text{OctONO} \xrightarrow{\text{TFA}} [\text{DONOR}, \text{NO}^+]\ \text{CF}_3\text{CO}_2^- + \text{OctOH} \qquad (2)$$

The IR spectral study of a range of methylbenzenes confirms the formation of methylbenzene–nitrosonium EDA complexes that are readily identified by the characteristic nitrosyl stretch in the range of 1870–2200 cm^{-1}. The actual frequency observed is dependent on the donor strength of the methylarene. Earlier studies with authentic methylbenzene–nitrosonium complexes showed that the more electron-rich arenes form stronger complexes and the increased electron donation results in a decrease in the IR stretching frequency of the nitrosonium moiety (4). The frequencies observed in this study are compared to those reported in Table 1.

The stretching frequencies of the nitrosonium moiety clearly track the ionization potentials of the methylbenzene as previously reported for the methylbenzene–nitrosonium EDA complexes [see Rathore et al. (4) as well Ref. (6)], confirming the identity of the complex.

Table 1. Vibration Spectra of Polymethylbenzene EDA Complexes from Octyl Nitrite and Trifluoroacetic Acid[a]

Methylbenzene	IP (eV)	*M*	υ_{EDA} (cm^{-1})	υ_{EDA} (cm^{-1})[b]	*A*[c]
Hexamethyl	7.85	0.1	1859	1862	0.40
Pentamethyl	7.92	0.5	1890	1896	1.02
1,2,4,5-Tetramethyl	8.05	1.0	1910	1912	1.15

[a] In dichloromethane solution with 0.5 *M* octyl nitrite and 0.5 *M* trifluoroacetic acid at 25°C.
[b] Comparative value of υ_{EDA} for [ArH, NO^+] NO_3^- in dichloromethane solution at −78°C from Ref. (8).
[c] Absorption at $\lambda_{\max}$.

Scheme 2.

As mentioned in Introduction previous studies have concluded that acidified mixtures of alkyl nitrites result in very low concentrations of protonated alkyl nitrites and that the protonated form reacts directly with nucleophiles present in the solution in order to transfer nitrosonium as described in Scheme 1. In our spectral studies of acidified solutions of octyl nitrite we find no evidence for nitrosonium in the absence of strong organic donor molecules. In contrast, the addition of relatively low concentrations of strong organic donors, such as hexamethylbenzene and butyl sulfide, induce the quantitative release of nitrosonium. A mechanism, which describes this, is shown in Scheme 2.

CONCLUSIONS

Electron-rich organic molecules affect the donor-induced release of nitrosonium from acidified solutions of alkyl nitrites in dichloromethane. The formation of highly colored organic donor–nitrosonium EDA complexes permits the spectroscopic identification and quantification of the released nitrosonium.

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REFERENCES

1. Williams, D.L.H. Adv. Phys. Org. Chem. **1983**, *19*, 381.
2. Aldred, S.E.; Williams, D.L.H. Fd. Chem. Toxicol. **1982**, *20*, 79.
3. Iglesias, E.; Garcia-Rio, L.; Leis, J.R.; Pena, M.E.; Williams, D.L.H. J. Chem. Soc., Perkin Trans. 2 **1992**, 1673.
4. Brownstein, S.; Gabe, E.; Lee, F.; Tan, L. J. Chem. Soc., Chem. Commun. **1984**, 1566; Brownstein, S.; Morrison, A.; Tan, L. J. Chem. Soc., Chem. Commun. **1984**, 1566; Borodskhin, G.I.; Nagi, S.M.; Gatilov, Y.V.; Mamatyuk, V.I.; Mudrakovskii, I.L.; Shubin, V.G. Dokl. Akad, Nauk. **1986**, *288*, 1364; Kim,

E.K.; Kochi, J.K. J. Am. Chem. Soc. **1991**, *113*, 4962; Rathore, R.; Lindemann, S.; Kochi, J.K. J. Am. Chem. Soc. **1998**, *120*, 1111.
5. Bosch, E.; Kochi, J.K. J. Org. Chem. **1995**, *60*, 3172.
6. Bosch, E.; Kochi, J.K. J. Org. Chem. **1994**, *59*, 5573; Lindemann, S.; Bosch, E.; Kochi, J.K. J. Chem. Soc., Perkin Trans. II, *submitted*.
7. Blatt, A.H., Ed. Org. Syn. **1943**, Coll. Vol. 2, 108, 204, 363.
8. Bosch, E.; Kochi, J.K. Res. Chem. Intermed. **1993**, *19*, 828; Bosch, E.; Kochi, J.K. J. Org. Chem. **1994**, *59*, 3314–25.

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