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INTERACTION OF ELECTRON ACCEPTORS WITH BASES—III[1]

THE ABSORPTION SPECTRA OF SUBSTITUTED POLYNITROBENZENES IN LIQUID AMMONIA

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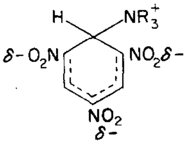
Abstract—The visible region absorption spectra of a series of substituted polynitrobenzenes in liquid ammonia have been measured. It is suggested that the absorption is produced by the respective pentadienyl anion formed by the attachment of the amide ion to the ring carbon atom of the polynitrobenzene which is *ortho* or *para* to the maximum number of nitro groups. Such structures have been proposed by Bunnett as intermediates in aromatic nucleophilic substitution reactions. Of the compounds studied primary and secondary aromatic nitro-anilines are exceptional, in that ionization appears to occur by loss of a proton from the amino group.

SOLUTIONS of polynitroaromatic compounds with aliphatic amines, either in the presence or absence of a third component, are often intensely coloured. Comparison has been made between these reactions and those which involve aromatic amines.[1–4] In many cases with aliphatic amines the absorption in the visible region alters with time. There is not as yet complete agreement between various workers as to the nature of the *initial* coloured product formed from the interaction of 1,3,5-trinitrobenzene and aliphatic amines in solvents of relatively low ionizing power. Miller and Wynne-Jones[2] suggest a charge-transfer complex; Briegleb *et al.*[4] propose an ion pair. We[1] have suggested that the product is a complex formed between the amine molecule and the 1,3,5-trinitrobenzene molecule by a dative bond from the loan pair on the nitrogen of the amine molecule to the 2-position in 1,3,5-trinitrobenzene (1). For solvents of high ionizing power, in particular liquid ammonia, the same interaction may not obtain. Many aromatic polynitrocompounds when dissolved in liquid ammonia have been shown to have high electrical conductivity.[5–7] Different interpretations have been given of this observation. Garner *et al.*[8,9] detected no evolution of gas nor any



I

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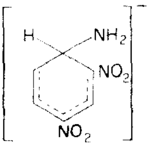
[1] Part II: R. Foster and R. K. Mackie, *Tetrahedron* **16**, 119 (1961).
[2] R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.* 2375 (1959).
[3] R. Foster, *J. Chem. Soc.* 3508 (1959).
[4] G. Briegleb, W. Liptay and M. Canter, *Z. Phys. Chem.* (*Frankfurt*) **26,** 55 (1960).
[5] E. C. Franklin and C. A. Krauss, *J. Amer. Chem. Soc.* **27,** 181 (1905).
[6] E. C. Franklin *Z. Phys. Chem.* **69,** 272 (1909).
[7] C. A. Krauss and W. C. Bray, *J. Amer. Chem. Soc.* **35,** 1343 (1913).
[8] M. J. Field, W. E. Garner and C. C. Smith, *J. Chem. Soc.* **127,** 1227 (1925).
[9] W. E. Garner and H. F. Gillbe, *J. Chem. Soc.* 2889 (1928).

decomposition of the substrate when a solution of 1,3-dinitrobenzene in liquid ammonia was electrolysed. They noted that the coloured ion migrated to the anode. From these observations they concluded that the reaction between solvent and solution must be:

$$C_6H_4(NO_2)_2 + 2NH_3 \rightleftharpoons C_6H_4(NO_2)_2 \cdot 2NH_3 \rightleftharpoons C_6H_4(NO_2)^{--} + N_2H_6^{++}$$

More recently Farr *et al.*[10] have repeated this particular electrolysis and they did observe an evolution of hydrogen at the cathode (and nitrogen at the anode) with partial reduction of the nitrocompound. It is therefore possible that the cation is the ammonium ion, and they suggested that the reaction between liquid ammonia and 1,3-dinitrobenzene gives rise to the ion II:



II

$$2NH_3 + C_6H_4(NO_2)_2 \rightleftharpoons \qquad + NH_4^+ \qquad (2)$$

Lewis and Seabourg[11] suggested that there is attachment of an ammonia molecule to the 2-position in 1,3,5-trinitrobenzene and in 1,3-dinitrobenzene, the product being stabilized by double chelation to the two nitro groups *ortho* to the point of attachment. Whether or not such chelation is significant, the product would be non-ionic and it would be difficult to account for the observed electrical conductivity.

We have measured the absorption spectra of a series polynitro- and substituted polynitro-benzenes dissolved in liquid ammonia in an attempt to resolve the various possibilities for the structures of the coloured products.

RESULTS

All the bands observed are broad and in general the maxima may not be determined to within less than ± 2mμ.

Solutions of 1-x-substituted-2,4,6-trinitrobenzenes (III, x = F, Cl, Br, I, OMe, OC_6H_5, NO_2) in liquid ammonia initially show two maxima, the higher energy band being the more intense. The spectra change with time. Superficially the higher energy band appears to grow at the expense of the lower energy band. However this often involves a considerable shift in wavelength (Table 1). With all these spectra there is finally a single band at 423–430 mμ. This approximately corresponds with the band for picramide in liquid ammonia (425 mμ), the small shifts in wavelength may be the result of absorption by traces of other products. In every case picramide has been obtained as the major product from the ammoniacal solution. With III (x = F, OMe) the reaction is so fast that only an inflexion is observed for the lower energy transition. Solutions of 1,3,5-trichloro-2,4,6-trinitrobenzene initially show one maximum and an inflexion at longer wavelengths. The spectrum rapidly changes to that corresponding to the triamino compound which was isolated quantitatively from the solution.

For solutions of III (x = CH_3) the secondary reaction is very much slower. On

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[10] J. D. Farr, C. C. Bard and G. W. Wheland, *J. Amer. Chem. Soc.* **71**, 2013 (1949).

[11] G. N. Lewis and G. T. Seaborg, *J. Amer. Chem. Soc.* **62**, 2122 (1940).

immediate evaporation of the solvent, 2,4,6-trinitrotoluene is recovered. In time the longer wavelength band increases in intensity, with long-standing solutions, no 2,4,6-trinitrotoluene could be recovered. With III (x = C_6H_5) the initial spectrum does not alter significantly with time, and after 12 hours the substrate may be recovered unchanged. With trinitro-*m*-xylene two maxima are observed, however in this case the longer wave transition is the more intense. With time both bands intensify. Trinitro-*m*-xylene may be recovered from the solution by immediate evaporation, but if the solution is allowed to stand for several hours before evaporation, no substrate could be detected. Trinitromesitylene appeared to be completely insoluble in liquid ammonia and it gave no colour. Solutions of 1,3,5-trinitrobenzene itself in liquid ammonia also show two maxima (460 mμ, 523 mμ), the longer wavelength transition being the more intense. The spectrum changes in time to a single broad maximum at $\sim$ 460 mμ. Addition of sodamide or ammonium chloride did not alter the initial or the final spectrum.

Table 1. Absorption maxima in the visible region of solutions of x-substituted 2,4,6-trinitrobenzenes in liquid ammonia

λ_1 and λ_2 are the initial maxima, λ_3 are the maxima which have developed after 18 hr

x	λ_1 (mμ)	λ_2 (mμ)	λ_3 (mμ)
1-H	460	523	450[a]
1-F	422	475[b]	427
1-Cl	450	514	429
1-Br	453	502	429
1-I	466	516	429
1-OCH_3	444	490[b]	430
1-OC_6H_5	443	502	429
1-NO_2	425	480	425
1-CH_3	458	523	521
1-C_6H_5	457	543	—
1-NH_2	425	—	—
1-$NHCH_3$	430	—	—
1-$N(CH_3)_2$	441	—	—
1-$N(C_2H_5)_2$	443	—	—
1,3-diCH_3	413	480	414[c]
1,3,5-triCl	433	500[b]	412
1,3,5-triNH_2	413	—	—

[a] Very broad maximum; [b] plateau or inflexion rapidly decreasing in intensity with time; [c] second broad maximum at 625 mμ.

The spectra of picramides (III, x = NH_2, NHMe, NMe_2) in liquid ammonia show little difference in their visible spectra from the picramides alone in alcoholic solution. Picramide was shown by Krauss and Bray[7] to give an electrically conducting solution in liquid ammonia (λ_∞ = 243 ohms^{-1} cm). Comparison of III (x = NH_2, NHMe, and NMe_2) in liquid ammonia indicates that the secondary amine has a comparable conductivity and that the tertiary amine has about half the conductivity of picramide.

In general the spectra of the substituted 1,3-dinitrobenzenes and certain mononitrobenzenes show only one maximum in the visible (Table 2); the exceptions are the

1-x-substituted-2,4-dinitrobenzenes (IV, x = Cl, Br, I) and 2,6-dinitroanisole. The band(s) develop slowly. In the case of 1,3-dinitrobenzene, sodamide was added to solution in liquid ammonia. This was found to increase the rate of development of the band but not to affect its position. Likewise addition of ammonium chloride reduced the rate of development, or at sufficiently high concentrations reduced the absorption to zero. This effect had previously been observed by Shatenshtein and Izrailavich.[12]

DISCUSSION

Three modes of ionization are considered: (a) electron transfer; (b) proton transfer; (c) formation of a polynitro-pentadienyl anion.

The interaction of 1,3-dinitrobenzene with liquid ammonia appears to be unaccompanied by any further interaction. After 24 hours it has been possible to recover the total amount of 1,3-dinitrobenzene from the solution by evaporation of the solvent. The residue was completely colourless, and had a m.p. of 91° which was not depressed by pure 1,3-dinitrobenzene. No E.S.R. absorption could be detected with a saturated solution in liquid ammonia. This seems to eliminate the possibility that the colour is the result of free radical formation, such as has been postulated by Miller and Wynne-Jones[2,13] in the case of certain trinitrobenzene aliphatic amine interactions.

In contrast to reactions in alcoholic solution where apparently analogous reactions of 1,3,5-trinitrobenzene with the stronger base OH^- have been shown not to involve proton transfer,[2,14] such reactions in liquid ammonia must be considered. Thus Shatenshtein *et al.*[15] have shown that there is significant proton transfer between 1,3-dinitrobenzene and liquid ND_3. The rate of exchange is increased by the presence of sodamide. Presumably NH_3 acts as a proton acceptor to become NH_4^+. This would explain the enhancement of the rate of increase of optical absorption observed in the interaction of 1,3-dinitrobenzene and liquid ammonia by the action of the more effective proton acceptor NH_2^-, and the reversal by the addition of NH_4^+. It is possible that with the stronger Lewis acid, 1,3,5-trinitrobenzene, the equilibrium is so far over in favour of complex formation that addition of NH_2^- or NH_4^+ does not significantly affect the concentration of the $C_6H_2(NO_2)_3^-$ ion. It has been assumed for a considerable time that ionization of picramide in liquid ammonia is the result of proton loss from the amino group. To account for the ionization of III (x = NMe_2) by proton transfer, one might propose that a proton is lost from a ring C-H as would be the case with the di- or tri-nitrobenzene.

The regularity of the initial spectra of the ring methylated trinitrobenzenes compared with those compounds in which the methyl groups are absent, suggests that proton transfer from the methyl group does not occur, at least initially. By contrast, the reaction of these compounds with strong alkali in alcoholic solution have been shown by Caldin and Long[16] to involve proton transfer from the methyl group.

However, although proton exchange has been demonstrated in such a typical system, this in itself is no proof that the anion is formed by the loss of a proton from 1,3,5-trinitrobenzene. Indeed Briegleb *et al.*[4] have shown that in the system piperidine

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[12] A. I. Shatenshtein and E. A. Izrailevich, *Acta Physicochim. U.R.S.S.* **12,** 73 (1940).

[13] R. E. Miller and W. F. K. Wynne-Jones, *Nature, Lond.* **186,** 149 (1960).

[14] J. A. A. Ketelaar, A. Bier and H. T. Vlaar, *Rec. Trav. Chim.* **73,** 37 (1954).

[15] A. I. Shatenshtein, N. M. Dykhno, E. A. Izrailevich, L. N. Vasil'eva and M. Faĭvush, *Dokl. Akad. Nauk. U.S.S.R.* **79,** 479 (1951).

[16] E. F. Caldin and G. Long, *Proc. Roy. Soc.* **A228,** 263 (1955).

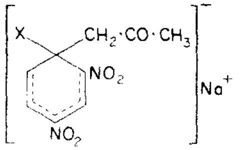
plus 1,3,5-trinitrobenzene in acetonitrile, which has many features in common with 1,3,5-trinitrobenzene in liquid ammonia, there is no evidence of proton transfer. The catalytic effect of NH_2^- and the reversed effect by NH_4^+ on the development of the absorption band of 1,3-dinitrobenzene in liquid ammonia may also be explained satisfactorily in terms of the formation of a pentadienyl anion by the addition of NH_2^- to the nitrocompound as had been suggested by Farr *et al.*[10] (II). Furthermore, there is a close correlation between the frequencies of the absorption bands of all the substituted 2,4-dinitrobenzenes in liquid ammonia measured (except those indicated in Table 2), and the frequencies of the absorption bands of the Janovsky complexes of the same nitrocompounds with acetone in the presence of sodium hydroxide; this includes primary and secondary 2,4-dinitroanilines. Structures of the type V have

TABLE 2. ABSORPTION SPECTRA IN THE VISIBLE REGION OF X-SUBSTITUTED 2,4-DINITROBENZENES
λ_1 are the maxima in liquid ammonia, λ_2 are the maxima of the Janovsky complexes

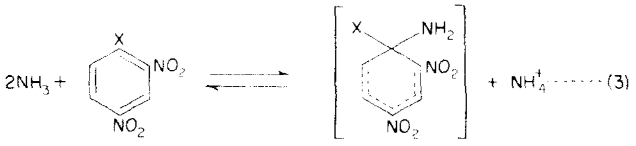
No.	X	λ_1 (mμ)	λ_2 (mμ)
1	1-H	564	570
2	1-C_6H_5	563	563
3	1-NH_2	538	526
4	1-$NHCH_3$	550	566
5	1-NHC_2H_5	551	566
6	1-$N(CH_3)_2$	555	565
7	1-piperdyl	562	567
8	1-OH(O^-)	430	415
9	1-OCH_3	552	563
10	1-OC_6H_5	553	563
11	1-$NHCOCH_3$	436	423
12	1-$OOCCH_3$	432	416
13	1-$OOCC_6H_5$	431	417
14	1-F	542[a,b]	557; 636
15	1-Cl	552; 642	549; 665
16	1-Br	552; 641	548; 664
17	1-I	552; 657	552; 675
18	4,6-diF	511[b,c]	589
19	4,6-diCl	617	640
20	4,6-diBr	627	645
21	4,6-diOC_6H_5	569	552
22	1,3-diCl	532	518
23	1,3,5-triCl	524	—[d]
24	3-NH_2	449	460
25	3-OCH_3	460,[b] 525	525
26	6-NH_2	423	—[e]
27	6-OCH_3	588	572
28	6-OH(—O^-)	468	445
29	6-COOH(—COO^-)	562	571

[a] Inflexion at ~640 mμ, rapidly decreasing in intensity with time; [b] point not plotted in Figure 1; [c] subsequent fast chemical reaction, intensity in the region 600 mμ decreases rapidly with time; [d] subsequent chemical reaction, colour changes from pink to yellow before any measurements could be made; [e] acetone layer rapidly darkened when shaken with sodium hydroxide.

been assigned[17–19] to the Janovsky complexes. By analogy the reactions with liquid ammonia would be:



V



(3)

VI

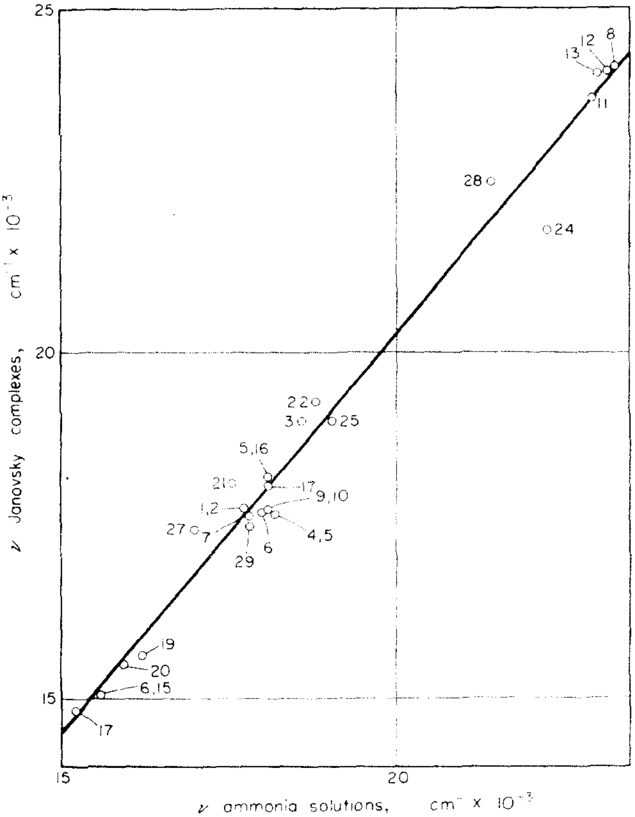


FIG. 1. Frequencies (ν) of absorption maxima of substituted 2,4-dinitrobenzenes in liquid ammonia, against the frequencies of the absorption maxima of the Janovsky complexes with acetone of the same substituted 2,4-dinitrobenzenes. The numbers refer to the compounds listed in Table 2.

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[17] T. Canback, *Farm. Revy.* **48**, 153, 234 (1949).

[18] T. Abe, *Bull. Chem. Soc. Japan* **32**, 778 (1959).

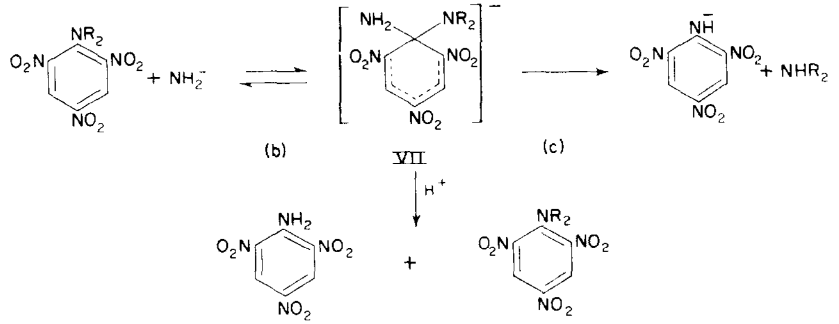
[19] M. Akatsuka, *J. Pharm. Soc. Japan* **80**, 378, 384, 389 (1960).

In liquid ammonia solutions of IV (x = F, Cl, Br, I, OMe, OC_6H_5, NO_2) where nucleophilic substitution in position 2 by $-NH_2$ is observed finally, the complex observed would correspond to the intermediate complex postulated by Bunnett[20–22] for such aromatic nucleophilic substitution reactions.

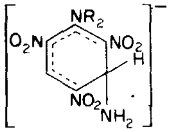
This conclusion is in general agreement with the observations of Briegleb *et al.*[4] who studied the system piperidine (PH) and 1,3,5-trinitrobenzene (T) in acetonitrile ($\epsilon = 38$). They concluded that the main species present were the ions TP^-, PH_2^+, $P_2H_3^+$ and the ion pair (TP^-, PH_2^+). From our work it is not possible to decide whether or not a cation $N_2H_7^+$, corresponding to $P_2H_3^+$ is present as well as NH_4^+, or of the importance of ion pair formation.

With polynitroanilines this particular mechanism cannot obtain. It may be assumed, as suggested above, that primary and secondary 2,4,6-trinitroanilines ionize by loss of a proton from the amino group. In the case of the tertiary amines, if the complex were to correspond to VII i.e.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \quad (a)$$



one would expect to obtain some unsubstituted picramide either on evaporation of the solvent, or preferably on acidification (in order to avoid possible consequences of the greater volatility of ammonia over the tertiary amine) by analogy with the decomposition of Meisenheimer[23] compounds on acidification. Indeed in the presence of the large excess of ammonia used in the experiment, one might expect the complete conversion to unsubstituted picramide by the mass action effect apart from the probable irreversibility of reaction *c*. In fact the original pure tertiary amine is always completely recovered. This suggests that no complex such as VII is formed in which the $-NH_2$ and the $-NR_2$ groups are symmetrically disposed. It is possible that solutions of N,N-dialkyl picramides in liquid ammonia form the anion by attack of NH_2^- on the 3-position to give VIII,



VIII

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[20] J. F. Bunnett and R. E. Zahler, *Chem. Rev.* **49**, 297 (1951).

[21] J. F. Bunnett, *Quart. Rev.* **12**, 1 (1958).

[22] J. F. Bunnett and J. J. Randall, *J. Amer. Chem. Soc.* **80**, 6020 (1958).

[23] J. Meisenheimer, *Liebigs Ann.* **323**, 205 (1902).

EXPERIMENTAL

Liquid ammonia I.C.I. 99·98% pure anhydrous ammonia was used without further treatment. Nitrocompounds were purified by recrystallization to constant melting point.

Solutions for the Janovsky reaction were obtained by dissolving 10^{-4} g of the nitrocompound in 25 ml acetone, which was then shaken with 25 ml 10 N sodium hydroxide for 2 min. The layers were allowed to separate for 10 min before the absorption spectrum of the acetone layer was measured.

The spectra in liquid ammonia were measured at ca. −40° and atmospheric pressure using a CF4R Optica recording spectrophotometer. The solutions were contained in an all-glass permanently-evacuated version of the vacuum jacketed cell described by Passerini and Ross.[21]

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[21] R. Passerini and I. G. Ross, *J. Sci. Instr.* **30**, 274 (1953).