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The Crystal Structure of a Carbanion. Potassium 4,4-Dinitro-2-butenamide

James R. Holden[1] **and Charles Dickinson**

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Abstract: The crystal structure of the potassium salt of the 4,4-dinitro-2-butenamide carbanion has been determined by X-ray diffraction. The entire carbanion is essentially planar. The N–C–N bond angle is 120° in spite of an O–O distance of only 2.51 Å between the nitro groups. The carbanions lie in planar layers 3.0 Å apart and are doubly hydrogen bonded into chains within these layers. The potassium cations lie 0.7 Å above and below the anion planes.

Nitromethane is a much stronger carbon acid than methane. However, unlike other acidifying groups, the effects of a second and third nitro group are not additive (see Table I). This lack of additivity has been attributed to steric repulsions which prevent all the atoms of the resulting carbanion from lying in the same plane.[2]

Table I. pK_a in Water at 25°[a]

CH_3NO_2	11	CH_3CN	25	$CH_3SO_2CH_3$	23
$CH_2(NO_2)_2$	4	$CH_2(CN)_2$	12	$CH_2(SO_2CH_3)_2$	14
$CH(NO_2)_3$	0	$CH(CN)_3$	−5[b]	$CH(SO_2CH_3)_3$	0

[a] See ref 2. [b] R. H. Boyd, *J. Phys. Chem.*, **67**, 737 (1963).

The thermodynamic acidity of a carbon acid (measured by the pK_a) is a function of the relative stability of the undissociated molecule and of the carbanion which results from deprotonation. A nitro group increases the acidity of methane both by stabilizing the carbanion and by decreasing the stability of the neutral molecule. Its stabilizing effect on the methide ion is due chiefly to delocalization of the charge by p-orbital interaction. Maximum interaction requires that the p orbitals of the carbon and nitrogen atoms be parallel, that is, that the sp^2 hybrid orbitals be coplanar. Therefore, two or three nitro groups can exert their full stabilizing effects only if the entire carbanion is coplanar.

Nitro groups make methane less stable toward deprotonation by withdrawing electrons from the carbon atom and thus weakening the C–H bond. Trinitromethane (nitroform) should be less stable than carbomethoxydinitromethane (methyl dinitroacetate) because the nitro group has a stronger electron-withdrawing effect than the carbomethoxy group. This estimate is based on the σ^* values of 2.00 listed by Taft[3] for carbomethoxy and 3.9 which can be derived for nitro from other values given by Taft.[3] From other values given in this compilation,[3] we estimate a σ^* value of 0.6 for the carbomethoxyvinyl group; therefore, carbomethoxyvinyldinitromethane (methyl 4,4-dinitro-2-butenoate) should be more stable than methyldinitroacetate and much more stable than nitroform.

As would be predicted from the proposed stabilities of the neutral molecules, nitroform is about 1.0 pK unit stronger an acid than methyl dinitroacetate.[4] However, 4,4-dinitro-2-butenoic acid derivatives are as strong or stronger acids than nitroform (see Table II). This would indicate that these compounds form more stable carbanions than either nitroform or methyl dinitroacetate.

Table II. pK_a in Methanol[4]

$(NO_2)_2CHCH{=}CHCOOCH_3$	3.15
$(NO_2)_2CHCH{=}CHCN$	1.91
$(NO_2)_3CH$	3.22

As stated above, a major factor in carbanion stability is delocalization of the charge from its formal location on the carbon atom. The reactivity of a carbanion toward an α,β-unsaturated system in a Michael-type addition gives an indication of the extent of such delocalization because the nucleophilicity of the carbanion is a function of the charge remaining on the carbon atom. Both trinitromethide and carbomethoxydinitromethide react readily with methyl acrylate in a Michael-type addition, but carbomethoxyvinyldinitromethide is totally unreactive.[4,5] This is additional evidence for the greater stability of the carbomethoxyvinyldinitromethide carbanion and indicates that the reason for its stability is extensive charge delocalization.

An obvious explanation for this carbanion stability (due to efficient charge delocalization) would be that 4,4-dinitro-2-butenoic acid derivatives form planar carbanions permitting maximum resonance interaction by

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(1) Author to whom inquiries should be addressed.

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both nitro groups and by the double bond. However, this conclusion does not agree with that drawn by Kamlet and Glover[6] from a study of the ultraviolet spectra of these compounds. A determination of the crystal structure of the potassium salt of 4,4-dinitro-2-butenamide was undertaken to determine whether the anion does indeed assume a planar configuration. From such a structure we hoped to learn something about the balance between the steric effects (favoring nonplanarity) and the electronic effects (favoring planarity). The amide was chosen for crystallographic convenience since it forms a stable crystal with a unit cell of desirable size and shape.

Experimental Section

A sample of potassium 4,4-dinitro-2-butenamide containing suitable crystals was prepared as described previously.[7] The dimensions of the triclinic cell were determined from oscillation and Weissenberg films with the crystal rotated about the *a* and *c* axes: $a = 4.55_7 \pm 0.01$ Å, $b = 8.31_1 \pm 0.01$ Å, $c = 9.89_8 \pm 0.01$ Å, $\alpha = 96° 3' \pm 20'$, $\beta = 87° 12' \pm 20'$, $\gamma = 100° 55' \pm 20'$. These values give a calculated density of 1.93 g/cc with two molecules per cell. The density as determined by flotation in a methylene iodide–tetrachloroethylene solution is 1.90 g/cc.[8]

Intensities were collected with the crystal rotating about the *a* axis. Levels 0*kl* through 4*kl* were collected using a Nonius integrating Weissenberg camera operating in a two-directional integration mode. Four-film packs were used and levels 1*kl* through 4*kl* were collected at relative spindle axis settings of 0 and 180° to eliminate the need for an oversize integration area to accommodate the expanded spots on half of the film. The intensities were read using a semiautomatic microdensitometer designed and built at this laboratory. The densitometer scanned in the θ direction, and the optical density difference between the peak height and interpolated background was correlated with exposure by means of a known gray scale. Of the 1479 reflections in the region of reciprocal space measured (Cu Kα, 1.5418 Å), 1095 had measurable intensity.

Determination of Structure

All calculations for the determination of this structure were performed on an IBM 7090 using the crystallographic computing system X-ray 63.[9]

The intensities within each film pack were correlated giving greater weight to those measurements in the middle of the intensity range. The two film packs for each of the levels 1*kl* through 4*kl* were correlated using reflections common to both packs. The intensities were corrected for absorption by Burnham's method.[10] These corrected intensities were then converted to structure factors.

Quasi-normalized structure factors (Karle–Hauptman *E*'s)[11] were calculated using form factors for the neutral species C, O, N, and H and the ionic species K^+ as given in the "International Tables for X-Ray Crystallography."[12] The average values for $|E|$ and $|E^2 - 1|$ from this calculation (Table III) indicated the centric space group P$\bar{1}$.

A sharpened, origin-removed Patterson calculation from the normalized structure factors ($\epsilon E^2 - 1$) clearly indicated the position of the potassium ion. An electron density map using phases determined from the potassium position indicated positions for the nonhydrogen atoms of the carbanion. Fourier and full-matrix least-squares refinement using individual, isotropic temperature factors produced a structure with an agreement factor (R) of 0.15. At this point, reflection ($11\bar{2}$) was omitted from the refinement. Although this reflection had the largest observed intensity, its calculated structure factor was more than twice its observed value. The reflection intensity is either measured too small because it exceeds the response of the film or is reduced by secondary extinction. Least-squares refinement with anisotropic temperature factors then lowered R to 0.089. The four hydrogen atoms of the carbanion were placed by assuming that all of the atoms are trigonal, that H_1 lies on the line between N_1 and O_1' of the adjacent carbanion (a linear hydrogen bond), and that the bond distances are all 1.075 Å. Inclusion of the hydrogen atoms lowered R to 0.085, but their positions were not stable when an attempt was made to include them in the least-squares refinement. Therefore the final four cycles of refinement were carried out with the hydrogen positions generated as indicated by the positions of the heavy atoms. In the final cycle the R value was 0.085, and the maximum shift/error ratio was 0.0009.

Table III. Average Values of Normalized Structure Factors

	$\lvert E \rvert$	E^2	$\lvert E^2 - 1 \rvert$
Observed	0.814	1.000	0.939
Theoretical for centric[11]	0.798	1.000	0.968
Theoretical for acentric[11]	0.886	1.000	0.736

The data were grouped by Weissenberg level (all reflections with the same Miller index *h*) and a scale factor assigned to each level. These level scale factors were determined during the early cycles of least-squares refinement using isotropic temperature factors. They were not included in the final refinement because of the high correlation which would exist between the scale factors and the B_{11} component of the anisotropic temperature factors.[13] This procedure could introduce or mask an over-all anisotropic trend in the temperature factors; therefore, any such trend may have no physical reality.

In all least-squares refinements, the quantity minimized was $\Sigma w(F_o - F_c)^2$, where w is the weight assigned to the reflection. For unobserved reflections, $(F_c - F_{\min})^2$ was included in the sum when the calculated structure factor, F_c, was greater than $F_{\min}$, the structure factor calculated from the minimum observable intensity. No contribution was included for unobserved reflections when F_c was smaller than $F_{\min}$. The weight was 1.0 for reflections with F_{rel} less than 10.0 and $(10.0/F_{\mathrm{rel}})^2$ for reflections with F_{rel} greater than 10.0.

The final atomic parameters are given in Table IV. The numbers in parentheses are the errors in the last digits as indicated by the inverse matrix from the last least-squares cycle. The anisotropic temperature factors are of the form

$$\exp[-\tfrac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$$

These B_{ij} values are on the same scale as the isotropic B values listed for the hydrogen atoms.

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Table IV. Atomic Parameters

	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K^+	0.3706 (3)	0.1161 (2)	0.3592 (1)	2.71 (6)	2.69 (6)	2.26 (5)	1.13 (5)	−0.72 (4)	−0.13 (4)
C_1	−0.0862 (13)	0.2260 (7)	0.0863 (6)	1.79 (25)	1.42 (20)	2.26 (22)	0.83 (17)	−0.09 (17)	−0.36 (16)
C_2	−0.1674 (13)	0.3873 (6)	0.1329 (5)	2.14 (25)	1.24 (19)	1.84 (21)	0.99 (17)	−0.28 (17)	−0.40 (15)
C_3	−0.0263 (12)	0.4761 (6)	0.2404 (6)	1.80 (24)	1.24 (19)	1.95 (21)	0.62 (16)	−0.10 (16)	−0.32 (16)
C_4	−0.0499 (12)	0.6339 (6)	0.3069 (6)	1.70 (23)	1.29 (19)	1.91 (21)	0.65 (16)	−0.38 (16)	−0.56 (16)
N_1	−0.2257 (12)	0.1497 (6)	−0.0236 (5)	2.57 (24)	1.40 (18)	2.73 (21)	1.03 (16)	−0.90 (17)	−1.00 (15)
N_2	0.1270 (11)	0.6897 (6)	0.4184 (5)	2.03 (21)	1.28 (17)	1.74 (18)	0.57 (14)	−0.10 (14)	−0.86 (14)
N_3	−0.2350 (11)	0.7320 (6)	0.2632 (5)	1.65 (20)	1.35 (17)	2.41 (20)	0.73 (14)	0.19 (15)	−0.31 (15)
O_1	0.0999 (12)	0.1690 (5)	0.1435 (4)	4.75 (26)	1.71 (17)	2.61 (19)	2.00 (17)	−1.53 (17)	−1.15 (14)
O_2	0.2994 (10)	0.6032 (5)	0.4543 (4)	2.64 (20)	2.12 (17)	2.14 (17)	1.20 (14)	−0.55 (14)	−0.29 (13)
O_3	0.1168 (11)	0.8265 (5)	0.4856 (5)	3.41 (23)	1.97 (18)	3.24 (21)	1.21 (15)	−1.04 (16)	−1.79 (15)
O_4	−0.2486 (11)	0.8715 (5)	0.3177 (5)	4.07 (25)	1.57 (17)	3.84 (22)	2.03 (16)	−1.10 (18)	−1.25 (15)
O_5	−0.3911 (10)	0.6726 (5)	0.1642 (5)	2.42 (20)	2.26 (18)	3.15 (20)	1.09 (15)	−1.03 (15)	−0.61 (15)
H_1	−0.1795	0.0328	−0.0676	2.20					
H_2	−0.3864	0.2053	−0.0690	2.20					
H_3	−0.3344	0.4324	0.0822	2.20					
H_4	0.1325	0.4174	0.2839	2.20					

A table of observed and calculated structure factors has been deposited with the American Documentation Institute.[14]

Discussion

A significant feature of the crystal structure of potassium 4,4-dinitro-2-butenamide is the planarity of the anion in spite of what should be large steric effects. The equation of the least-squares plane[15] through the carbon, nitrogen, and oxygen atoms listed in Table IV is

$$-2.903x - 2.988y + 6.030z = 0.0897$$

where x, y, and z are fractional coordinates in the triclinic cell. The standard deviation of these atoms from the plane is 0.027 Å. The distances (in angstroms) of the individual atoms of the anion from the plane are C_1 through C_4: −0.006, −0.040, −0.014, −0.011; N_1 through N_3: 0.024, 0.003, 0.008; and O_1 through O_5: 0.019, 0.022, −0.030, 0.057, −0.026 (see Figure 1 for atom designations). Since the maximum estimated error in the position of an atom is 0.006, some of the deviations from coplanarity are surely real; however, we feel that no deviation is large enough to be chemically significant.

The interatomic distances within the anion are given in Figure 1. The estimated standard deviations of the distances between atoms range from 0.007 to 0.009 Å. The planar configuration of the anion produces several short nonbonded distances: 2.512 Å between O_3 and O_4, 2.653 Å between C_3 and O_2, 2.723 Å between C_3 and O_5, and 2.737 Å between C_2 and O_5.

The bond angles are given in Figure 2. Their standard deviations range from 0.5 to 0.6°. Angle C_3–C_4–N_3 is significantly larger than angle C_3–C_4–N_2, and angle C_2–C_3–C_4 is significantly larger than the normal C—C=C range, apparently to relieve the crowding in the surrounding parts of the anion. The unusually small bond angle C_1–C_2–C_3 may result from the close packing of the anions to be discussed later.

The bond lengths in the amide group, C_1–O_1 and C_1–N_1, are about average when compared to lengths of equivalent bonds reported for the compounds listed in Table V.[16–30] The lengths of bonds C_1–C_2 and C_2–C_3 are not significantly different from the values given by Dewar and Schmeising[31] for single and double bonds between sp^2 carbon atoms, 1.479 and 1.353 Å, respectively. Therefore, the configuration found for the amide end of the anion is not different from that found in neutral molecules.[32]

Table V. Bond Distances in Amides (Angstroms)

	C–N	C–O
Formamide[16]	1.30	1.255
Acetamide[17]	1.38	1.28
Decanamide[18]	1.312	1.282
Tetradecanamide[19]	1.26	1.23
Oxamide[20]	1.315	1.243
Succinamide[21]	1.333	1.238
Glutaramide[22]	1.34	1.22
l-Adipamide[23]	1.33	1.23
Suberamide[24]	1.32	1.25
Benzamide[25]	1.31	1.24
Nicotinamide[26]	1.34	1.22
Picolinamide[27]	1.322	1.234
α-Pyrazinamide[28]	1.312	1.244
Glutamine[29]	1.28	1.27
Glycyl-L-asparagine[30]	1.39	1.22

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(14) The structure factor table has been deposited as Document No. 9511 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C.

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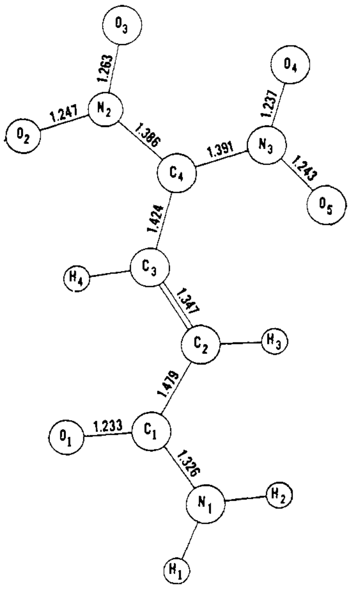

Figure 1. Bond lengths.

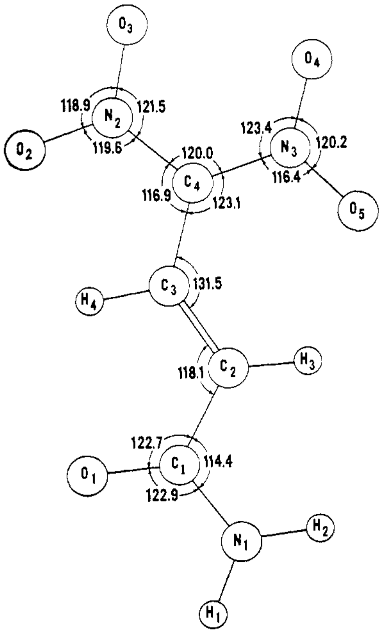

Figure 2. Bond angles.

The coordination of atom C_4 is trigonal. It lies only 0.008 Å from the plane defined by C_3, N_2, and N_3. This is less than twice the standard deviation of the atom positions and corresponds to an angle of only 0.4° between the bonds to C_4 and this plane. Therefore, the configuration at C_4 is not significantly nonplanar. Certainly there is no evidence in dinitrobutenamide of the 3° nonplanarity reported for the carbanions ammonium tricyanomethide[33] and pyridinium dicyanomethide.[34]

The two nitro groups lie close to the plane of the trigonal C_4 atom. The distances of oxygen atoms O_2 through O_5 from the plane defined by C_3, N_2, and N_3 are 0.035, −0.035, 0.039, and −0.033 Å. Thus the N_2 and N_3 nitro group planes make angles of only 1.9 and 2.0° with the trigonal carbon plane. These small angles indicate that the carbon and nitrogen atoms are oriented properly for p-orbital interaction, and that the nitro groups can contribute to delocalization of the charge formally assigned to C_4. The fact that the bond between C_2 and C_3 lies close to the C_4 plane indicates that C_3 is also oriented properly for p-orbital interaction.

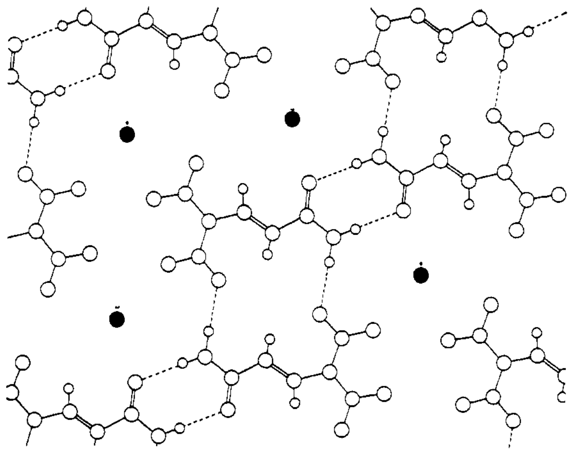

Figure 3. Arrangement of atoms within a layer of the structure.

The length of C_3–C_4 is significantly shorter than the value given by Dewar and Schmeising[31] for a single bond between sp^2 carbon atoms, 1.479 Å. The lengths of C_4–N_2 and C_4–N_3 are not significantly different from each other or from the length reported for the similarly situated C–N bond in dipotassium nitroacetate.[35] These bonds are significantly shorter than the C–N bonds found between nitro groups and aromatic rings, which average about 1.47 Å.[36–39] However, they are longer than many of the C–N bonds found between amine groups and aromatic rings and those found in amide groups (Table V). We believe that the C_4–N_2 and C_4–N_3 bond lengths should be compared with those found for other nitro groups. On this basis the bond lengths given in Figure 1 indicate that the charge on the carbanion is delocalized from its formal location on C_4 into the nitro groups and into the bond to C_3.

The crystal structure of potassium 4,4-dinitro-2-butenamide shows that in the solid state the dinitrobutenamide carbanion can assume a planar configuration which allows efficient charge delocalization. If the anion also assumes this stable configuration in solution, it would explain why dinitrobutenamide is a relatively strong carbon acid.[4] However, it would contradict some of the explanations which have been given for the nonadditivity of the effects of nitro groups based on nonplanarity of carbanions.[1,6,40]

The dinitrobutenamide anions are packed in the crystal lattice in planar layers 3.0 Å apart. Figure 3 shows the arrangement of the anions within each layer. As indicated, the anions are doubly hydrogen bonded into continuous chains within the layers. Both hydro-

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gen atoms of the amide group are involved: one in a bond to the amide oxygen atom of the anion located at $(-x, -y, -z)$ with an N–O distance of 2.93 Å and the other in a bond to O_5 of the anion located at $(-1 - x, 1 - y, -z)$ with an N–O distance of 2.97 Å.

(Note: If bond angle C_1–C_2–C_3 had a more usual value, *i.e.*, 122°, while C_3, C_4, and the nitro groups maintained their positions and the bond distances and angles of the amide group remained normal, this N–O separation would be only 2.81 Å. Therefore, intermolecular crowding probably causes angle C_1–C_2–C_3 to assume the unusually small value of 118.1°.)

Double hydrogen bonding between amide groups has been found in the following compounds: formamide,[16] decanamide,[18] tetradecanamide,[19] oxamide,[20] succinamide,[21] glutaramide,[22] suberamide,[24] benzamide,[25] picolinamide,[27] and α-pyrazinamide.[28] The N–O distance found for dinitrobutenamide, 2.93 Å, is about equal to the average value from these other amide structures, 2.94 Å. The nitro group hydrogen bond in potassium dinitrobutenamide has the same N–O separation as the average value found for the intermolecular amine to nitro group bonds in the strongly bonded compounds, 1,3-diamino-2,4,6-trinitrobenzene[37] and 1,3,5-triamino-2,4,6-trinitrobenzene.[38]

The potassium cations lie 0.7 Å above (+) and below (−) the anion planes (Figure 3). The eight shortest distances between anion atoms and the potassium position listed in Table IV are listed in Table VI. These atoms do not form an obvious coordination pattern. Using the atomic radii listed by Pauling[41] (1.40 Å for O and 1.33 Å for K^+), the van der Waals contact distance would be 2.73 Å. The only potassium distance which was found to be shorter than this involves O_1, the amide group oxygen. If this is a charge interaction, it is further evidence of delocalization of the charge on the carbanion from its formal location on C_4. In any event, the atomic distribution shows that potassium 4,4-dinitro-2-butenamide forms an ionic solid.

Table VI. Shortest Distances to the K^+ Ion

Anion atom	Anion position	Distance, A
O(1)	(x, y, z)	2.633
O(3)	$(-x, 1 - y, 1 - z)$	2.726
O(3)	$(1 - x, 1 - y, 1 - z)$	2.796
O(3)	$(x, -1 + y, z)$	2.852
O(4)	$(1 + x, -1 + y, z)$	2.899
O(2)	$(1 - x, 1 - y, 1 - z)$	3.024
O(4)	$(x, -1 + y, z)$	3.167
O(4)	$(-x, 1 - y, 1 - z)$	3.214

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The Electrochemical Reduction of Aromatic Azo Compounds

Joe L. Sadler and Allen J. Bard[1]

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712.

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Abstract: The electrochemical behavior of a series of aromatic azo compounds in dimethylformamide solutions was studied by polarography, cyclic voltammetry, controlled-potential coulometry, electron spin resonance spectroscopy, and ultraviolet spectroscopy. The electrochemical reduction of these compounds is generally similar to that of the aromatic hydrocarbons in aprotic media. The reduction occurs in two one-electron steps. The product of the first electron transfer is a stable anion radical. The second electron transfer to the dianion is followed by a chemical reaction producing a protonated species which is oxidizable to the parent azo compound. The product of the second electron transfer also produces the corresponding arylhydrazine in a following reaction.

Although the electrochemical reduction of azobenzene and related compounds has been studied extensively, relatively few studies of the reaction in aprotic media have been reported. Aylward, Garnett, and Sharp[2] recently reported the ac and dc polarographic reduction of azobenzene in dimethylformamide (DMF) solutions. They proposed that azobenzene is reduced in a rapid one-electron transfer reaction to the anion radical and in a second slow electron transfer to produce a stable dianion.

The aim of this investigation was to study the electrochemical reduction of a series of aromatic azo compounds in DMF using a variety of electrochemical techniques, so that a general mechanism for the reduction of these compounds could be formulated. A further aim is to obtain electrochemical data, *e.g.*, reduction potentials, which can be correlated with electron spin resonance (esr) spectroscopic results and molecular orbital calculations, as has been accomplished with aromatic hydrocarbons.

The compounds studied in this investigation are given below.

The voltammetric behavior of these compounds in

(1) To whom correspondence and requests for reprints should be directed.

(2) G. G. Aylward, J. L. Garnett, and J. H. Sharp, *Anal. Chem.*, **39**, 457 (1967).