Results and Discussion

The least-squares linear regression equations of X *vs.* σ^*, as shown in Figures 1 and 2, gave eq 3 and 4.

$$X_{\mathrm{eq}\,1} = 0.37\sigma^* + 2.06 \qquad (3)$$

$$X_{\mathrm{eq}\,2} = 0.26\sigma^* + 2.30 \qquad (4)$$

The standard deviation from regression ($S_{X\cdot\sigma^*}$) was 0.17 for eq 3 and 0.12 for eq 4. The Student "t" test gave $t = 6.18$ and 6.24, respectively, both of which have $p < 0.01$ for 11 degrees of freedom. The correlation coefficient is 0.88 for both equations.

It can be seen from Table II that, in almost all cases, agreement with previous electronegativity values is quite good. Of the 44 groups examined only groups 10, 12, 13, 19, 21, 27, and 29 differ significantly ($p < 0.05$) from X_{H} values and of these only groups 12, 13, and 21 differ significantly from X_{H} at the 0.01 level. Table II also illustrates the principle that the group electronegativity is mainly due to the contribution of the first atom and to a smaller extent from the contribution of the second atom. Huheey has made note of the fact that the assumption of perfect electronegativity equalization gives equal "weight" to all atoms in the group, but, in reality, the electronegativity of a group is always influenced most by the atom which links the group to the remainder of the molecule.[15c] With this in mind, it is felt that the X_{H} values of groups 21, 27, and 29 are most likely overestimates and that the X_{H} values of groups 10, 12, 13, and 19 may also be somewhat on the high side.

Although Robinson's criticism[10d] of the work of Bell, *et. al.*,[10b] is probably correct, and his omission of the fluorine compounds from the equation is justified, the result is really not significant in the determination of group electronegativity. The $X_{\mathrm{eq}\,2}$ values only differ from the $X_{\mathrm{eq}\,1}$ values by 10% for the very low σ^* values and are nearly identical for σ^* values >1.50. Thus it is felt that either eq 3 or eq 4 can be used to give a good estimate of group electronegativity.

The Reduction of Methyl Viologen by Cyanohydrin Anions

DAVID N. KRAMER, GEORGE G. GUILBAULT, AND F. MARION MILLER

Physical Research Laboratory, Research Laboratories, U. S. Army Edgewood Arsenal, Edgewood Arsenal, Maryland, and Department of Pharmaceutical Chemistry, University of Maryland, Baltimore, Maryland

Received May 4, 1966

In order to elucidate the mechanism of oxidation of cyanohydrin anions, the character of the methyl viologen reduction by these anions was investigated. The over-all rate of the reaction was governed by the rate of formation of the cyanohydrin anions ($k_1 = 4 \times 10^3$ l. mole^{-1} min^{-1}). A stoichiometric ratio of two methyl viologen cation radicals was produced per molecule of cyanohydrin consumed. It is concluded that *p*-cyano- and *p*-nitrobenzaldehydecyanohydrin anions reduce methyl viologen to the radical cation by a one-electron-transfer process.

In a previous report,[1] it was shown that the cyanohydrin anions of *p*-nitrobenzaldehyde and *p*-cyanobenzaldehyde reduce 1,2-dinitrobenzene to *o*-nitrophenylhydroxylamine. The possibility existed that the reduction is effected *via* hydride transfer, as in the case of the Cannizzaro reaction,[2] or by electron transfer to yield radical anions as exemplified by the numerous citations of Russell,[3,4] or alternatively that a transfer of a hydrogen atom may be involved in the reduction step. Attempts to study the cyanohydrin anions *per se* were unsuccessful. The cyanohydrin anion of *p*-nitrobenzaldehyde collapses to form a variety of azo-, azoxy-, and nitrosobenzoic acids,[5] while the cyanohydrin anion of *p*-cyanobenzaldehyde yields the corresponding benzoin derivative which, in the presence of the cyanohydrin anions, is reduced to the deoxybenzoin with the concomitant formation of *p*-cyanobenzoic acid and an unidentified viscous oil.[6] Since the cyanohydrin anions are not amenable to direct measurement, it was considered feasible to study their reaction with known one electron acceptors, *e.g.*, the viologens,[7] *via* an interception technique.

The viologen (I) upon interception of an electron, is converted to the highly colored and stable free radical (III), which may be measured spectrophotometrically. The reaction is depicted in Scheme I.

This report deals with the evidence in support of Scheme I and the significance thereof.

Results and Discussion

Table I summarizes the results of semiquantitative experiments run to determine the reaction in alkaline solution of *p*-nitro- and *p*-cyanobenzaldehyde with methyl viologen and 2,3,5-triphenyltetrazolium chloride (TTC) in the presence and absence of cyanide ion. The reaction of other reductants is also included. It can be seen that while ascorbate and benzoin anions reduce methyl viologen and TTC directly, *p*-nitro- and *p*-cyanobenzaldehyde in alkaline medium require cyanide ion for the reduction.

A kinetic study of the reaction of *p*-cyanobenzaldehyde, cyanide ion, and methyl viologen revealed first-order dependance on *p*-cyanobenzaldehyde and cyanide ion and a zero-order dependance on methyl viologen (Table II), similar to what was observed in the reaction of *p*-nitrobenzaldehyde, cyanide, and 1,2-dinitrobenzene.[1] The rate was measured by following the change with time of the absorbance at 600 mμ. The molar absorptivity of the methyl viologen radical cation, used to calculate the rates in Table II, was 1×10^4.[7] The reaction kinetics are in consonance with Scheme I, where $k_1 >> k_{-1}$ and less than k_2, k_3, and k_4

---

[1] D. N. Kramer and G. G. Guilbault, *J. Org. Chem.*, **31**, 1103 (1966).

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, Book Co., Inc., New York, N. Y., 1940, pp 350–352.

[3] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4143, 4155 (1962).

[4] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

[5] G. Heller, *Ber.*, **46**, 285 (1913).

[6] J. H. Ashley, H. J. Buber, A. Ewins, G. Newberry, and A. D. Self, *J. Chem. Soc.*, 114 (1942).

[7] E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, **86**, 5527 (1964).

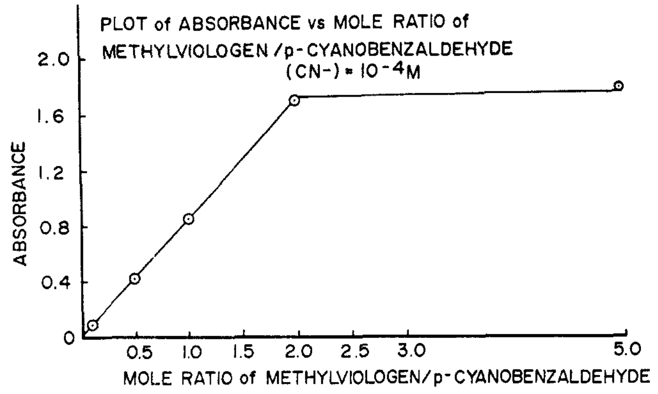


Figure 1.

TABLE I

REACTION OF *p*-NITRO- AND *p*-CYANOBENZALDEHYDE AND OTHER REDUCTANTS WITH ONE-ELECTRON ACCEPTORS

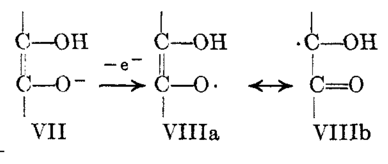
One-electron acceptors, aldehyde/reductant[a]	0.01 *M* CN⁻ added, ml	Electron[b] acceptor	Resultant[c] color	Time for color appearance
p-Nitrobenzaldehyde	0	MV	Yellow-brown	2–3 min
p-Nitrobenzaldehyde	1.0	MV	Blue	Immediate
p-Cyanobenzaldehyde	0	MV	Nc	. . .
p-Cyanobenzaldehyde	1.0	MV	Blue	Immediate
Ascorbate	0	MV	Blue	Immediate
Benzoin	0	MV	Blue	10 min
Benzoin	1.0	MV	Blue	Immediate
p-Nitrobenzaldehyde	0	TTC	Nc	. . .
p-Nitrobenzaldehyde	1.0	TTC	Red	Immediate
p-Cyanobenzaldehyde	0	TTC	Nc	. . .
p-Cyanobenzaldehyde	1.0	TTC	Red	Immediate
p-Me_3N^+-benzaldehyde iodide	0	MV	Nc	. . .
p-Me_3N^+-benzaldehyde iodide	1.0	MV	Blue	Slow

[a] One milliliter of 0.1 *M* aldehyde (or reductant) in methoxyethanol; 0.2 ml of 0.5 *M* NaOH added. [b] One milliliter of MV (methyl viologen) or TTC (triphenyltetrazolium chloride), 0.1 *M*, in distilled water. [c] Nc, no color.

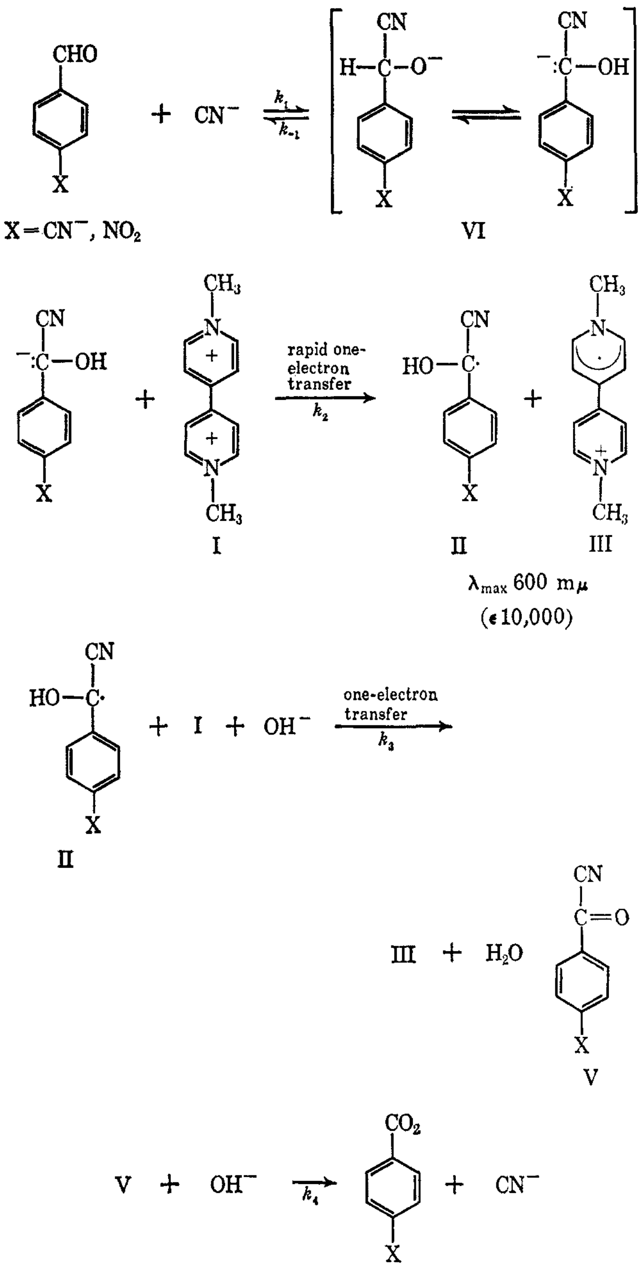
(which are all fast reactions and indistinguishable), and $k_1 = 4 \times 10^3$ l. mole^{-1} min^{-1}.

From the results reported above, and reasoning by analogy, it is possible to deduce the character of the oxidation step of Scheme I. Thus methyl viologen which has been shown[7] to undergo one-electron reduction in the formation of the radical cation (III), is consumed in the reaction under study, in a 2:1 molar ratio with respect to the cyanohydrin anion. In addition, TTC, which has been demonstrated to participate in one-electron reductions,[8,9] serves readily as an electron acceptor from the cyanohydrin anion.

Examination of other structures (ascorbic acid[10] and benzoin[11]) show the presence of the enediol anion (VII) capable of undergoing one-electron oxidation to produce a resonance-stabilized radical (VIII).



SCHEME I



Analogously, the cyanohydrin anion of *p*-cyanobenzaldehyde (VI) by one-electron oxidation would form a radical (II), stabilized by electron delocalization over both the α-cyano group and the *p*-cyanophenyl substituent.[12] Thus, precedence for free-radical stabilization by an α-cyano group is found in the case of the decomposition of azoacetonitriles[13] and radical ad-

---

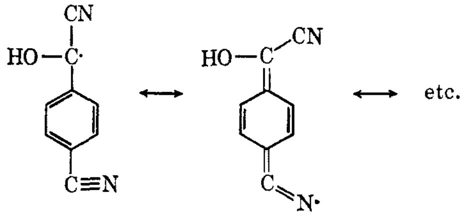
(8) B. Jambor, *Acta Chem. Akad. Sci. Hung.*, **4**, 55 (1954); *J. Chem. Soc.*, 1609 (1958).

(9) O. W. Meander and G. A. Russell, *J. Org. Chem.*, **31**, 442 (1966).

(10) A. Weissberger and J. E. LuValle, *J. Am. Chem. Soc.*, **66**, 700 (1944).

(11) A. Weissberger, H. Mainz, and E. Strasser, *Ber.*, **62**, 1942 (1929).

(12) Note that the free-radical stabilization may be attributable to delocalization over the *p*-cyanophenyl and cyano moieties.



(13) Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 725.

TABLE II

KINETICS OF THE REACTION INVOLVING METHYL VIOLOGEN, p-CYANOBENZALDEHYDE, AND CYANIDE ION (T = 25°)

A. [Methyl Viologen] = 4.0×10^{-2} M; [OH^-] = 10^{-1} M; [CN^-] = 5×10^{-5} M

[p-Cyanobenzaldehyde], M	Initial rate[a] × 10^5
5×10^{-5}	1.0
1×10^{-4}	2.1
2.5×10^{-4}	5.0
5.0×10^{-4}	10.1
2.5×10^{-3}	51.0

B. [p-Cyanobenzaldehyde] = 4.0×10^{-2} M; [OH^-] = 10^{-1} M; [CN^-] = 5×10^{-5} M

[Methyl viologen], M	Initial rate[a] × 10^5
1×10^{-4}	73
1×10^{-3}	73
1×10^{-2}	74
1×10^{-1}	80

C. [p-Cyanobenzaldehyde] = 4.0×10^{-2} M; [OH^-] = 10^{-1} M; [Methyl Viologen] = 4×10^{-2} M

[Cyanide], M	Initial rate[a] × 10^5
2.5×10^{-6}	4.0
5.0×10^{-6}	7.0
1.0×10^{-5}	15
2.0×10^{-5}	35
5.0×10^{-5}	80

[a] Initial rates expressed as moles per liter per minute; rate = $k_1[CN^-][p\text{-cyanobenzaldehyde}]$; $k_1 = 4 \times 10^3$ l. mole^{-1} min^{-1}.

ditions to acetonitrile.[14] Similarly, stabilization of a benzyl radical substituted in the *para* position with electron-withdrawing groups is reported in studies of the dissociation of hexa-p-nitrophenylethane.[15]

The requirement of the presence of the *para* electron-withdrawing substituent in the cyanohydrin in order to allow the formation of the radical *via* the corresponding cyanohydrin anion has been demonstrated.[1]

From the foregoing it may be inferred that the reduction of the 1,2-dinitrobenzene by p-cyano- and p-nitrobenzaldehyde cyanohydrin anions proceeds *via* one-electron steps. It would also appear likely that a similar mechanism obtains in the reduction of 1,2-dinitrobenzene by ascorbic acid, and phenylgloxal in alkaline medium. It is noteworthy that the reductive capacity of phenylglyoxal is markedly enhanced by addition of cyanide.[16,17]

Experimental Section

Benzoin and p-nitrobenzaldehyde, (Eastman Organics Co.) and p-cyanobenzaldehyde (Aldrich Chemical Co.) were dissolved in methoxyethanol to make 0.10 M solutions. A 0.1 M solution of ascorbic acid was prepared in water. Methyl viologen (British Drug House) and 2,3,5-triphenyltetrazolium chloride (Aldrich Chemical Co., 0.10 M) were made up in distilled water; p-formylphenyltrimethylammonium iodide was prepared by the method of Zaki and Tadros.[18] One milliliter of reductant was added to 1 ml of methyl viologen or TTC solutions and 0.2 ml of 0.5 M NaOH, and the color change with time was noted (Table I).

The order of dependance of the reaction of methyl viologen with p-cyanobenzaldehyde and cyanide was determined spectrophotometrically varying the concentration of each reactant while holding the others constant. All rates were calculated by dividing the change in optical density at 600 mμ/min (ΔA/min) by the molar absorptivity of the methyl viologen radical ion, 1×10^4.[7]

In order to ascertain the stoichiometry of the reaction, a plot of total absorbance *vs.* mole ratio of methyl viologen to p-cyanobenzaldehyde using excess cyanide ion, was made (Figure 1). A stoichiometric ratio of two methyl viologen radical cations for every one p-cyanobenzaldehyde was obtained, in conformity with Scheme I.

Registry No.—p-Nitrobenzaldehyde, 555-16-8; p-cyanobenzaldehyde, 105-07-7; benzoin,119-53-9; p-Me_3N^+-benzaldehyde iodide, 7541-76-6.

[14] Meerwein, Buchner, and Van Emster, *J. Prakt. Chem.*, **152**, 237 (1939); Rondesvedt and Vogel, *J. Am. Chem. Soc.*, **77**, 3069 (1955).

[15] F. L. Allen and S. Sugden, *J. Chem. Soc.*, 440 (1936).

[16] B. Gorlich, *Ber.*, **89**, 2145 (1956).

[17] V. Franzen, *ibid.*, **89**, 2154 (1956).

[18] A. Zaki and Wadie Tadros, *J. Chem. Soc.*, 350 (1941).

Molecular and Spectral Properties of α-Cyano-N-benzylidene Anils

JOHN W. LEDBETTER,[1] DAVID N. KRAMER,[2] AND F. MARION MILLER[3]

U. S. Army Chemical Research and Development Laboratory, Edgewood Arsenal, Maryland

Received August 18, 1966

A number of new α-cyano-N-benzylidene anils have been prepared by the reaction of nitrosophenol sodium salt, the appropriate pyridinium salt, and potassium cyanide. Electronic absorption spectra of these α-cyano anils show steric hindrance to coplanarity due to the cyano group. However, it was found that in spite of the steric feature the cyano group has an effect on infrared stretching frequencies, pK_a's of p-hydroxy derivatives, and the electronic $\pi \rightarrow \pi^*$ transitions. As a result of these effects, and others, one concludes that the steric hindrance to coplanarity is only intermediate at the most. If one extrapolates this conclusion to N-benzylideneaniline, there must be less than intermediate steric hindrance in this molecule.

The electronic absorption spectra of α-cyano-N-benzylidene anils show long wavelength bands of reduced intensity rather than of high intensity commonly associated with $\pi \rightarrow \pi^*$ transitions. In fact, the spectrum of N-benzylideneaniline, the parent structure, shows a reduced intensity for this band. There have already been efforts to establish reasons why this is so for N-benzylideneaniline while for stilbene and azobenzene the intensities are high. Jaffé, *et al.*,[4] have stated that this is due to a smaller transition moment for the less symmetrical N-benzylideneaniline. Heil-

[1] Department of Chemistry, Medical College of South Carolina, Charleston, S. C.

[2] U. S. Army Chemical Research and Development Laboratory, Edgewood Arsenal, Md.

[3] Department of Pharmaceutical Chemistry, University of Maryland, Baltimore, Md.

[4] H. H. Jaffé, S.-J. Yeh, and R. W. Garner, *J. Mol. Spectry.*, **2**, 120 (1958).