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ELECTROREDUCTION OF DIPHENYLDIAZOMETHANE IN ACETONITRILE AT A HANGING MERCURY DROP ELECTRODE

F. M. Triebe, James H. Barnes, M. Dale Hawley,* and Richard N. McDonald*
Department of Chemistry, Kansas State University, Manhattan, Kansas, 66506, USA

Abstract: Cyclic voltammetric studies of the reduction of diphenyldiazomethane (Ph_2CN_2) *in* CH_3CN-Me_4NPF_6 *at a hanging mercury drop electrode have established that the halflife of* $Ph_2CN_2^{\cdot -}$ *is less than 1 ms at either 8°C or -37°C.*

The electrochemical reduction of diphenyldiazomethane (Ph_2CN_2) in N,N-dimethylformamide (DMF) containing 0.1 $\underline{M}$ ($\underline{n}$-Bu)$_4$NClO$_4$ at a platinum cathode was reported to involve the intermediacies of both $Ph_2CN_2^{\cdot -}$ and $Ph_2C^{\cdot -}$.[1,2] Although $Ph_2CN_2^{\cdot -}$ was not directly observed on the cyclic voltammetric time scale, its presence was inferred by the formation of $Ph_2C{=}NNH_2$ when electroreduction of Ph_2CN_2 was effected in the presence of added proton donors. From these and other results, we concluded that $Ph_2CN_2^{\cdot -}$ reacted principally by rapid loss of molecular nitrogen to give the carbene anion radical, $Ph_2C^{\cdot -}$. The principal reaction products, $Ph_2C{=}N{-}N{=}CPh_2$ and Ph_2CH_2, were proposed to arise by a chain reaction in which Ph_2CH^- is the chain carrying species (eqs. (1)-(9)):

$$Ph_2CN_2 + e^- \rightleftarrows Ph_2CN_2^{\cdot -} \qquad (1)$$

$$Ph_2CN_2^{\cdot -} \xrightarrow{HA,e^-} Ph_2C{=}N\bar{N}H + A^- \qquad (2)$$

$$Ph_2CN_2^{\cdot -} \xrightarrow{-N_2} Ph_2C^{\cdot -} \xrightarrow{H^+,e^-} Ph_2CH^- \qquad (3)$$

$$Ph_2CH^- + Ph_2CN_2 \rightarrow Ph_2CH\bar{N}N{=}CPh_2 \qquad (4)$$

$$B + Ph_2CH\bar{N}N{=}CPh_2 \rightarrow BH^+ + Ph_2C{=}N{-}N{=}CPh_2^{\,2-} \qquad (5)$$

$$Ph_2C{=}N{-}N{=}CPh_2^{\,2-} + 2\ Ph_2CN_2 \rightarrow Ph_2C{=}N{-}N{=}CPh_2 + 2\ Ph_2CN_2^{\cdot -} \qquad (6)$$

$$Ph_2C{=}N\bar{N}H + Ph_2CN_2 \rightarrow Ph_2C{=}N\bar{N}CHPh_2 + N_2 \qquad (7)$$

$$Ph_2C{=}N\bar{N}H + HA \rightarrow Ph_2C{=}NNH_2 + A^- \qquad (8)$$

$$Ph_2\bar{C}H + HA \rightarrow Ph_2CH_2 + A^- \qquad (9)$$

where B = Ph_2CH^-, $Ph_2C^{\cdot -}$ or $Ph_2CN_2^{\cdot -}$, and HA = $Ph_2CH\bar{N}N{=}CPh_2$ or ($\underline{n}$-Bu)$_4N^+$

The stability of $Ph_2CN_2^{\cdot -}$ and its principal reaction mode (eq. 3) has recently been questioned.[3] Whereas we found that $Ph_2CN_2^{\cdot -}$ was too unstable ($\underline{t}_{1/2}$ < 1 ms) to give a discernible anodic peak on the reverse, positive-going sweep in a cyclic voltammetric experiment under all conditions examined (-51°C $\le \underline{T} \le$ 23°C; 0.5 V/s $\le \underline{v} \le$ 100 V/s; DMF, CH_3CN, and C_3H_7CN; ($\underline{n}$-Bu)$_4$NClO$_4$ and/or Me_4NPF_6),[1,2] Parker and Bethell[3] claim that Ph_2CN_2 is reduced reversibly at a mercury cathode in acetonitrile containing Me_4NBF_4. We will demonstrate in this communication that Parker and Bethell's observation is an artifact of their use of a mercury electrode surface for their electrochemical studies, and that their "reversible couple" is the fortuitous combination of two different redox processes.

The cyclic voltammetric behavior of Ph_2CN_2 at a hanging mercury drop electrode is illustrated in Figure 1, a-d. Under the conditions specified by Parker and Bethell for the observance of the reversible reduction of Ph_2CN_2 to $Ph_2CN_2^{\cdot -}$ ($\underline{T}$ = 8°C, a scan rate of 100 V/s, and a saturated CH_3CN solution of Me_4NPF_6), a cyclic voltammogram is obtained which resembles that expected for an electrochemically reversible one-electron process (Figure 1a). However, although the separation of 60 mV for $\underline{E}_p - \underline{E}_{p/2}$ for the cathodic wave is consistent with this interpretation, the 200 mV separation between the anodic and cathodic peak potentials greatly exceeds the expected value of approximately 60 mV. The fact that $Ph_2CN_2^{\cdot -}$ is not reversibly formed becomes obvious when the temperature is lowered. At -37°C and a scan rate of 100 V/s, the postpeak anodic current decreases approximately linearly with time whereas for a reversible system this current decreases by a more complex function involving $t^{\frac{1}{2}}$ (see Figures 1b and 1c). This anodic peak shape clearly demonstrates the effect of adsorption on the mercury surface. In addition, the separation between the anodic and cathodic peak potentials has increased to approximately 550 mV (Figure 1b). Kinetic behavior also becomes evident as the scan rate is decreased. At -37°C and a scan rate of 20 V/s, an absorption peak that occurs at the same potential as that for the irreversible oxidation of $Ph_2CH\bar{N}N{=}CPh_2$ appears near 0.1 V on the second positive-going half cycle (Figure 1c).

In addition to the claim by Parker and Bethell that $Ph_2CN_2^{\cdot -}$ can be observed directly by cyclic voltammetry in CH_3CN in the presence of Me_4N^+, they report that the cathodic peak potential for the reduction of Ph_2CN_2 is unaffected by the presence of electroinactive diethyl malonate (DEM). From this result, these workers concluded that the proton donor is not involved kinetically in the decomposition of $Ph_2CN_2^{\cdot -}$ under the reaction conditions, and that $Ph_2CN_2^{\cdot -}$ must undergo relatively slow, rate-determining hydrogen atom abstraction from acetonitrile. In our experiments, added DEM has a pronounced effect on the reduction of Ph_2CN_2 in CH_3CN as shown by comparing Figures 1a and 1d, the latter containing a 22-fold excess of DEM. The addition of DEM essentially eliminates the anodic peak at -0.7 V on the reverse, positive-going sweep, and a reversible couple appears near 0.4 V. Since this same couple can be made to appear by scanning in the positive-going direction from an initial potential of 0 V if a base such as Me_4NOH is added to a solution of DEM in CH_3CN-Me_4NPF_6 (saturated), the conjugate base of DEM must be generated as a result of the electroreduction of Ph_2CN_2 in the presence of DEM. The effects of temperature and proton donor not only disprove Parker and Bethell's assignment of the anodic peak at 0.7 V as being due to the reoxidation of $Ph_2CN_2^{\cdot -}$, but it also invalidates their attempt to relate the disappearance of this anodic adsorption peak to the kinetics of $Ph_2CN_2^{\cdot -}$ decomposition.

In contrast, when electroreduction of Ph_2CN_2 is effected on a platinum electrode surface under these conditions ($\underline{T}$ = 8°C, scan rate of 100 V/s, and CH_3CN-Me_4NPF_6 (saturated)), no adsorption is apparent and the cyclic voltammetric results are consistent with the interpretation which we presented previously for the reduction of Ph_2CN_2 in DMF.[1,2] As evidenced by the cyclic voltammogram in Figure 1e the reduction of Ph_2CN_2 on platinum is chemically irreversible at 8°C at our maximum scan rate of 100 V/s. Although the absence of an anodic wave for the oxidation of $Ph_2CN_2^{\cdot -}$ precludes a kinetic study of $Ph_2CN_2^{\cdot -}$ decomposition, it does establish a maximum halflife of 1 ms for $Ph_2CN_2^{\cdot -}$.[4] The only anodic wave discernible at this scan rate occurs near -0.35 V and is assigned to the irreversible oxidation of Ph_2CH^-, the observed reaction product of $Ph_2CN_2^{\cdot-}$.[2] The anodic peak for Ph_2CH^- is kinetically controlled and decreases in relative magnitude as the scan rate is decreased (Figure 1f). Concomitantly, an irreversible anodic peak appears near 0.2 V that is due to the oxidation of the intermediate product, $Ph_2CH\bar{N}N{=}CPh_2$, formed when Ph_2CH^- couples with Ph_2CN_2. The two principal products that were obtained by a coulometric reduction of Ph_2CN_2 at a platinum cathode in CH_3CN-Me_4NPF_6 (saturated) are $Ph_2C{=}N{-}N{=}CPh_2$ (42%) and Ph_2CH_2 (57%).

We suspect that Parker and Bethell's use of mercury may have contributed to the misinterpretation of these workers that $Ph_2CN_2^{\cdot-}$ has an appreciable lifetime in CH_3CN. The formation of organomercurials when mercury is used as the electrode material is well known (e.g., $(PhCH_2)_2Hg$ formation when $PhCH_2Br$ is reduced at a mercury cathode[5]) and may account for the anodic wave that appears near -0.7 V at 8°C in Figure 1a. A specific possibility is that Ph_2CH^- is oxidized to $Ph_2CH\cdot$ and that this radical then rapidly reacts with the mercury surface to form an organomercury species. The effect of this follow-up reaction would be to shift the Ph_2CH^- anodic wave to more negative potential.[4] Since decreasing temperature should also slow the rate of $Ph_2CN_2^{\cdot-}$ reaction, thereby causing the Ph_2CN_2 cathodic peak to shift negatively, Parker and Bethell perhaps arrived at a fortuitous set of conditions in which the irreversible reduction of Ph_2CN_2 and the irreversible oxidation of Ph_2CH^- in the presence of mercury appeared to constitute a chemically reversible system.

We also emphasize that our coulometric and product data preclude reaction pathways which involve extensive hydrogen atom abstraction by anion radical intermediates. For example, the electroreduction of Ph_2CN_2 in DMF-0.1 M $(n\text{-}Bu)_4NClO_4$ gives an n value of 0.30 and a product distribution of 87% $Ph_2C{=}N{-}N{=}CPh_2$, 1% $Ph_2C{=}O$, 9% Ph_2CH_2, 2% $Ph_2CHNHN{=}CPh_2$ and 0.6% $Ph_2C{=}NNH_2$.[2] If either $Ph_2CN_2^{\cdot-}$ or $Ph_2C^{\cdot-}$ were to hydrogen atom abstract, these hydrogens must ultimately be removed as protons from the coupled intermediate, $Ph_2CH\bar{N}N{=}CPh_2$, by the electrogenerated bases $Ph_2C^{\cdot-}$, Ph_2CH^-, $Ph_2C{=}NNH^-$, and $Ph_2CH\bar{N}N{=}CPh_2$ (see eqs. (1)-(9)). Because the combined yields of the last three products is less than 12% under these conditions, the anion radicals $Ph_2CN_2^{\cdot-}$ and $Ph_2C^{\cdot-}$ must instead proton abstract from $Ph_2CH\bar{N}N{=}CPh_2$ (eq. 5). Since Ph_2CH^-, *not* $Ph_2C{=}NNH^-$, is the first observable electroactive intermediate in the reduction of Ph_2CN_2, we conclude that $Ph_2CN_2^{\cdot-}$ reacts principally by rapid loss of nitrogen and that Ph_2CH^- is formed via the intermediacy of the carbene anion radical, $Ph_2C^{\cdot-}$, as shown in eq. (3).

Acknowledgments

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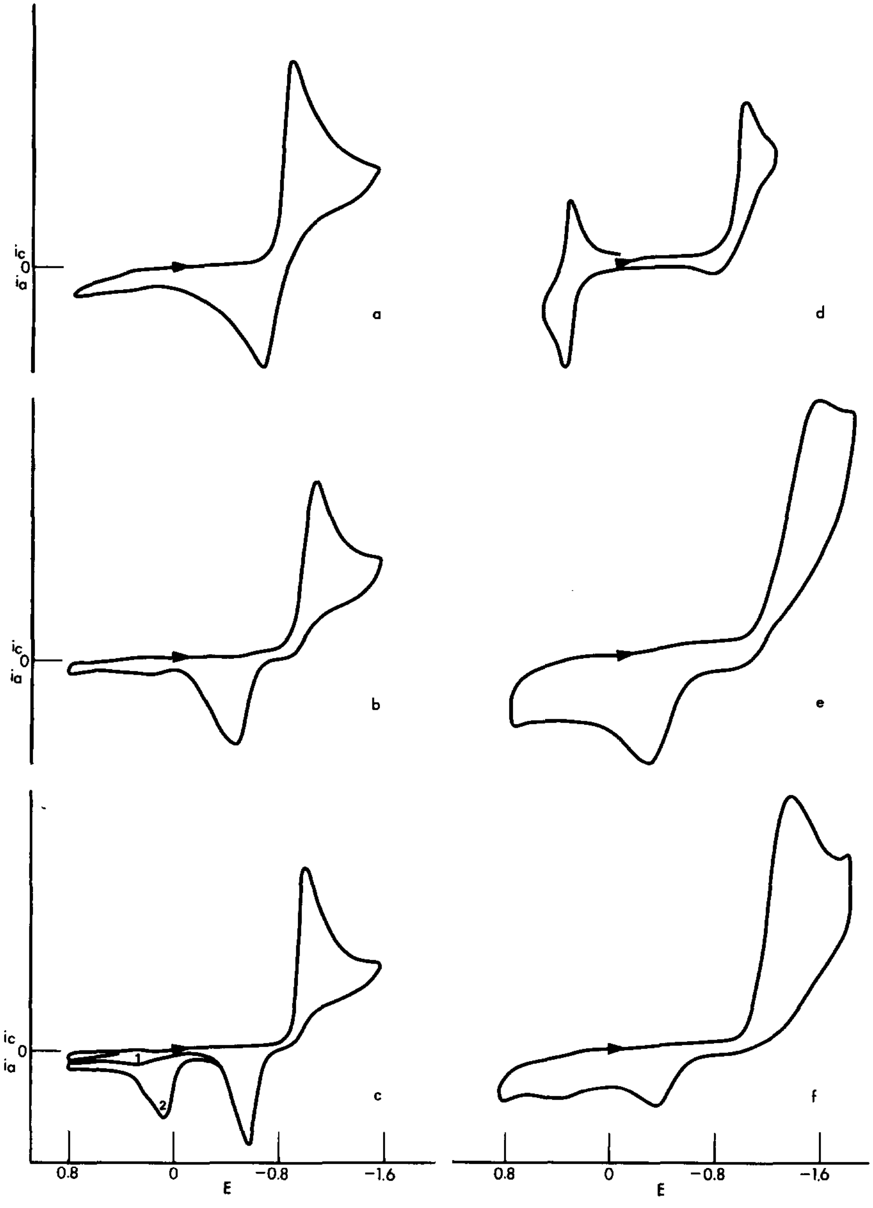

Figure 1 Cyclic voltammograms for the reduction of Ph_2CN_2 in CH_3CN under the following conditions: (a) $\underline{T}$ = 8°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), and hanging mercury drop electrode (HMDE); (b) $\underline{T}$ = -37°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated) and HMDE; (c) $\underline{T}$ = -37°C, $\underline{v}$ = 20 V/s, Me_4NPF_6 (saturated), and HMDE; (d) $\underline{T}$ = 8°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), DEM (89 m$\underline{M}$), and HMDE; (e) $\underline{T}$ = 8°C, $\underline{v}$ = 100 V/s, Me_4NPF_6 (saturated), and planar platinum electrode (0.25 cm^2); and (f) $\underline{T}$ = 8°C, $\underline{v}$ = 20 V/s, Me_4NPF_6 (saturated), and planar platinum electrode. The potential of the cadmium amalgam reference electrode is -0.75 V vs. saturated calomel electrode.

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