

Radical-anions and Dianions of Methylphenylacetylene. The Role of Dianions in Protonation and Electron-transfer Processes

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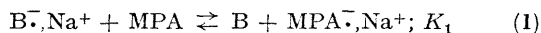
Summary: Kinetic and product studies show that electron transfer to methyl(phenyl)acetylene (MPA) gives its dianions ($\text{MPA}^{2-}, 2\text{Na}^+$) which are protonated by MPA yielding $\text{Ph}\bar{\text{C}}=\text{CHMe}, \text{Na}^+$ and $\text{Ph}\bar{\text{C}}=\text{C}=\text{CH}_2, \text{Na}^+$ as the products.

In a recent study of radical-ions and dianions of diphenylacetylene (DPA)^{1,2} we have shown that a highly unfavourable electron-transfer equilibrium which maintains a minute equilibrium concentration of dianions is responsible for the observed process. Our present studies of the electron-transfer reaction involving sodium biphenylide ($\text{B}^{\cdot-}, \text{Na}^+$) as a donor and methyl(phenyl)acetylene (MPA) as an acceptor have revealed again the importance of dianions.

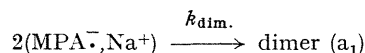
A solution in tetrahydrofuran of sodium biphenylide ($\text{B}^{\cdot-}, \text{Na}^+$) containing a large excess of biphenyl (B) was mixed in a stop-flow apparatus with a solution containing an excess of MPA. The reaction was followed spectrophotometrically by monitoring the optical density at 620 nm (λ_{max} of $\text{B}^{\cdot-}, \text{Na}^+$) and showed to be second order in $\text{B}^{\cdot-}, \text{Na}^+$. Plots of $1/[\text{B}^{\cdot-}, \text{Na}^+]$ vs. time (Figure 1) are strictly linear up to 95% conversion. However, the apparent second-order rate constants, k_b , derived from such plots depend on the concentrations of B and MPA (note that [B] and [MPA] remain constant during each individual run). The dependence of k_b upon [B] and [MPA] is shown in Figure 2 (see also Table); namely, $\log k_b$ varies linearly with $\log\{[\text{MPA}]/[\text{B}]\}$, the plot having a slope of 2. Hence, $-d[\text{B}^{\cdot-}, \text{Na}^+]/dt = \text{const.} [\text{B}^{\cdot-}, \text{Na}^+]^2 [\text{MPA}]^2 / [\text{B}]^2$.

Three mechanisms can account for these kinetic findings:

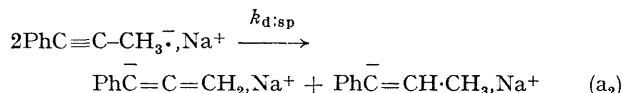
(a) A rapidly established equilibrium (1) maintains a



minute equilibrium concentration of MPA radical-ion ($\text{MPA}^{\cdot-}, \text{Na}^+$) which in turn either dimerize (mechanism a_1)



or disproportionate (mechanism a_2) the latter reactions



being the rate determining steps of the overall process.

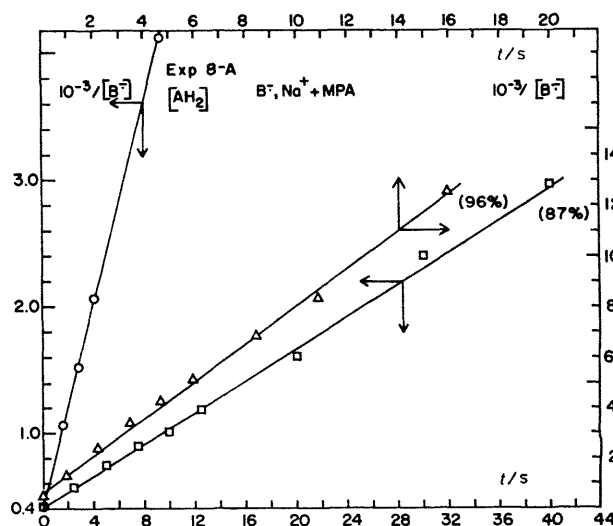
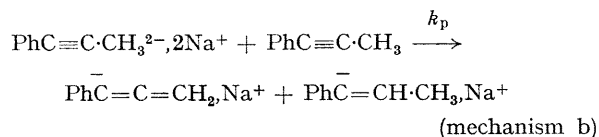


FIGURE 1. Typical second order plots ($1/[\text{B}^{\cdot-}, \text{Na}^+]$) for the reaction $\text{B}^{\cdot-}, \text{Na}^+ + \text{MPA} \rightarrow \text{products}$. The arrows on each line point to the scale in which it is plotted. Expt. 5 $[\text{MPA}] = 0.026\text{M}$, $[\text{B}] = 0.70\text{M}$, $[\text{B}^{\cdot-}, \text{Na}^+]_0 = 0.0025\text{M}$ plotted up to 96% conversion. Expt. 6 $[\text{MPA}] = 0.091\text{M}$, $[\text{B}] = 0.705\text{M}$, $[\text{B}^{\cdot-}, \text{Na}^+]_0 = 0.0018\text{M}$ plotted up to 87% conversion. Expt. 8a performed in the presence of AH_2 (0.020M) otherwise under similar conditions as Expt. 5, i.e., $[\text{MPA}] = 0.0234\text{M}$, $[\text{B}] = 0.76\text{M}$. (N.b. second-order character and the large increase in the rate resulting from the addition of AH_2 .)

(b) In addition to equilibrium (1), a second equilibrium (2)



maintains perhaps even smaller equilibrium concentration of the dianions, $\text{MPA}^{2-}, 2\text{Na}^+$, which are protonated in a rate determining step by MPA, *i.e.*,



The solution containing the reagents was protonated after completion of the process by adding methanol (this operation, like the previous one, was performed on a vacuum line). Dimeric products were not found, whereas β -methylstyrene and phenylallene were identified (n.m.r. spectra) as major products. The presence of β -methylstyrene was confirmed also by g.l.c.; however, phenylallene apparently polymerizes on the chromatographic column and could not be detected.†

The identification of the protonated products disproved mechanism (a₁) but these results do not discriminate between mechanisms (a₂) and (b).

TABLE

Run	[MPA]/M	[B]/M	[MPA]/[B]	Apparent bimolecular rate const. $k_b / (\text{M}^{-1} \text{s}^{-1})$
19	0.0118	0.605	0.0176	16.2
21	0.0105	0.316	0.029	38.0
13	0.026	0.624	0.040	75.0
12	0.051	0.705	0.0725	268.0
26	0.0092	0.089	0.095	490.0
6	0.091	0.705	0.129	760.0
22	0.057	0.093	0.615	16000 (flow only)

When necessary, k_b was calculated by using an integrated form which takes into account the decrease in MPA concentration resulting from the reaction.

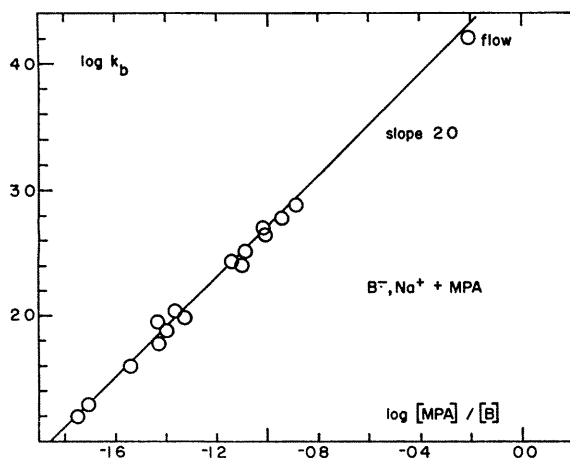


FIGURE 2. Plot of the log of the apparent bimolecular rate constant k_b vs. $\log [\text{MPA}]/[\text{B}]$. The point marked "flow" denotes the result obtained as the reagents flow through the optical cell.

† It is known that some allene derivatives easily polymerize when exposed to air.³

To discriminate between these two alternatives, we investigated the kinetics of the electron-transfer in the presence of an excess of dihydroanthracene (AH_2). In the absence of MPA a negligible fraction of $\text{B}^{\cdot-}, \text{Na}^+$ is protonated by AH_2 in one minute—the time needed to complete a kinetic run. The addition of AH_2 to MPA greatly accelerated the rate of the studied reaction (Figure 1). The reaction performed in the presence of AH_2 is *still* second order in $\text{B}^{\cdot-}, \text{Na}^+$ (Figure 1), and the respective apparent bimolecular rate constant k_b multiplied by $\{[\text{B}]/[\text{MPA}]\}^2$ varies linearly with $[\text{AH}_2]/[\text{MPA}]$ (Figure 3). Hence, in the presence of AH_2 the rate is given by $-d[\text{B}^{\cdot-}, \text{Na}^+]/dt = K_1 K_2 \{[\text{B}^{\cdot-}]^2 \cdot [\text{MPA}]^2 / [\text{B}]^2\} \{k_p + k_p' [\text{AH}_2]/[\text{MPA}]\}$; the optical spectrum of $\text{PhC}=\text{C}=\text{CH}_2$, observed in the absence of AH_2 , disappears, being replaced by the spectrum of AH^- .

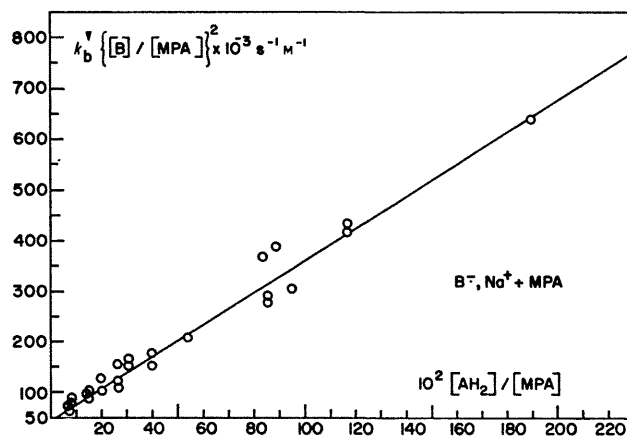


FIGURE 3. Plot of $k_b \{[\text{B}]/[\text{MPA}]\}^2$ vs. $[\text{AH}_2]/[\text{MPA}]$.

This result rules out the disproportionation mechanisms (a₂) according to which the rate of the reaction should not be affected by the addition of AH_2 , and confirms mechanism (b). Had the radical disproportionation been replaced by the protonation $\text{MPA}^{\cdot-}, \text{Na}^+ + \text{AH}_2 \rightarrow \text{MPAH} + \text{AH}^-, \text{Na}^+$ ($\text{AH}^- =$ monoprotonated anthracene dianion), then although the rate would be accelerated, as observed, it would be expected to be proportional to $[\text{B}^{\cdot-}, \text{Na}^+]/[\text{B}]$ and not $\{[\text{B}^{\cdot-}, \text{Na}^+]/[\text{B}]\}^2$ as demonstrated. Hence, dianions are present in the system and responsible for the reaction with dihydroanthracene. It is plausible, therefore, that mechanism (b) and not (a₂) is responsible for the reaction proceeding in the absence of dihydroanthracene. It is worth noting that mechanisms (a₂) and (b) cannot be distinguished by purely kinetic means, since their transition states have the same composition. The results obtained with dihydroanthracene lead to the ratio of k_p' to k_p of 6.7:1, *i.e.*, protonation of $\text{MPA}^{2-}, 2\text{Na}^+$ by AH_2 is 6.7 times faster than by MPA.

In conclusion, for weak acids, RH, the indirect protonation of radical-ions may be faster than a direct one, *e.g.*, $2\text{A}^{\cdot-} \rightleftharpoons \text{A}^{2-} + \text{A}$ followed by $\text{A}^{2-} + \text{HR} \rightarrow \text{AH}^- + \text{R}^-$ provides a more easy route to the products than $\text{A}^{\cdot-} + \text{HR}$

$\rightarrow \text{AH}\cdot + \text{R}^-$ followed by $\text{AH}\cdot + \text{A}^{\cdot-} \rightarrow \text{AH}^- + \text{A}$. The faster protonation of the extremely strong A^{2-} base may offset its lower concentration. Indeed, we found recently the protonation of perylenide radical-ions by methyl, ethyl, isopropyl, and t-butyl alcohol to proceed through their

dianions because the reaction is second order in radical-ions and retarded by the addition of perylene.⁴

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