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Reactivity and Mechanism for Aryl Carbenic Anion Radicals

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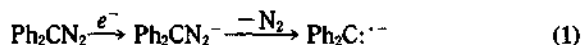
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Aryl carbenic anion radicals have been generated from the corresponding alkoxy-aryl diazo compounds by unimolecular decomposition reaction in various electrolyte/solvent systems. The electrochemical reductions of alkoxy-aryl diazo compounds in the electrolyte/solvent system are shown to initially be a one-electron process which affords the corresponding anion radicals. The unimolecular loss of nitrogen is favored at the propagation step and accelerated by the oxygen and carbon atoms of alkoxy group adjacent to the diazo function. The structure of the carbene anion radical in the termination is considered to be a resonance hybrid.

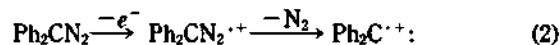
Introduction

Anion radicals of the carbene exist the intermediates in the electrochemical reduction of the diazoalkanes^{1,2}. Diphenylcarbene anion radical could be produced *via* one unimolecular loss of nitrogen from the corresponding diazodiphenylmethane radical ion Eq. (1)³. Decomposition reaction of



diazodiphenylmethane anion radical was of the first-order in acetonitrile and *N,N*-dimethylformamide⁴. The characteristic features of the unimolecular decomposition, (1), consist in that they have relatively high activation energies and take place only with extensive delocalization of a negative charge⁴.

However, the decomposition of aryldiazoalkanes by an electron-transfer chain catalysis reaction gave a carbene cation radicals in the presence of copper(II) salts with non-nucleophilic anions in aprotic solvents⁵.

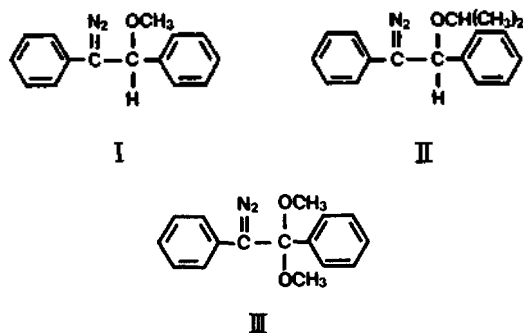


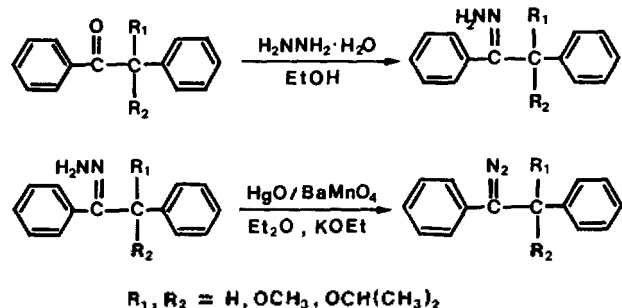
Those unimolecular decomposition reactions of aryldiazoalkanes could give different radicals depending upon the variation of the reaction conditions such as the presence of nucleophiles, the nature of electrolytes, and the presence of catalysts *etc.*

While the point of the question still remains unclear,

two independent studies have provided convincing kinetic evidences for the electrochemical generation of carbene anion radicals from the azibenzil⁶ and diethyl diazomalonate⁷. It was concluded that the kinetic results were consistent with initial generation to give the carbene anion radical. This may suggest that localization of the charge in the anion radicals into the carbonyl oxygen, facilitates the loss of dinitrogen atoms.

We now examine the influence of the alkoxy group in the reactions of various alkoxy-aryldiazo compounds (I, II, and III) by detection of the radicals employing generation by the method of electrochemical decomposition. We also report here the kinetic results for the reaction of electrochemical decomposition of aryl carbene anion radicals in various solvents and electrolytes.





Scheme 1.

Experimental

Materials. 2-Methoxy-1,2-diphenyl diazoethane(I), 2-isopropoxy-1,2-diphenyl diazoethane(II) and 2,2-dimethoxy-1,2-diphenyl diazoethane(III) were prepared from oxidation of the corresponding hydrazones⁵ with freshly prepared yellow mercuric oxide-barium manganate(VI) mixture dissolved in the saturated potassium hydroxide ethanol solution and diethyl ether (Scheme 1).

The products (I, II, and III) were isolated as a dark red oil; IR (NaCl, neat); 2060 ($C=N^+=N^-$) cm^{-1} ; ¹H-NMR ($CDCl_3$); δ 7.6-7.1 (m, 8H, ArH), 7.1-6.8 (m, 2H, ArH), 5.3 (s, 1H, -CH), 3.5 (s, 3H, -OCH₃) for I. IR (NaCl, neat); 2080 ($C=N^+=N^-$) cm^{-1} ; ¹H-NMR ($CDCl_3$); δ 7.5-6.7 (m, 10H, ArH), 5.5 (s, 1H, -CH), 3.9 (sep, $J=6.0$ Hz, 1H, -OCH(CH₃)₂), 1.3 (dd, $J=6.0$ Hz, 6H, -OCH(CH₃)₂) for II. IR (NaCl, neat); 2070 ($C=N^+=N^-$) cm^{-1} ; ¹H-NMR ($CDCl_3$); δ 7.6-7.4 (m, 2H, ArH), 7.4-6.6 (m, 8H, ArH), 3.1 (s, 6H, -C(OCH₃)₂) for III.

The purity of the diazo compound was checked by treatment with HBF₄ in methanol and with acetic acid in acetonitrile solution. All other compounds were commercially available and the compounds were recrystallized to give sharp melting points.

Constant Current Electrolyses. The glass vessel was fitted with a cylindrical smooth platinum working electrode with 50 cm² of surface area. It was also fitted with an auxiliary platinum electrode in a separate centrally located compartment connected by way of a sintered disc. The reaction vessel capacity was 80 cm³. The diazo compound (I, II, and III) solution (0.005 or 0.001 M) containing 0.1 M of tetramethyl ammonium tetrafluoroborate (Me₄NBF₄) as a supporting electrolyte in 50 cm³ of dry acetonitrile (MeCN) or dime-

thylsulphoxide (DMSO) was stirred and flushed with purified nitrogen and maintained at $-5^\circ C$ during the reaction. Other supporting electrolytes such as 0.1 M of tetraethyl ammonium tetrafluoroborate (Et₄NBF₄) or 0.1 M of tetrabutyl ammonium tetrafluoroborate (Bu₄NBF₄) in *N,N*-dimethyl formamide (DMA) were carried on according to the same method. A conventional constant current generator supplied current which was usually in the range of 0.1-30 mA. Samples of the reaction mixture (ca. 0.2 cm³) were withdrawn at the time intervals by a syringe through a septum cap on one of the ports of the electrolysis vessel. The samples then were analysed immediately in a CaF₂ cell and the concentration of the diazo compound determined from the intensity of the IR peak at ca. 2060 cm^{-1} using a calibration curve constructed using solutions of known concentrations. Data processing was carried out with an on-line computer.

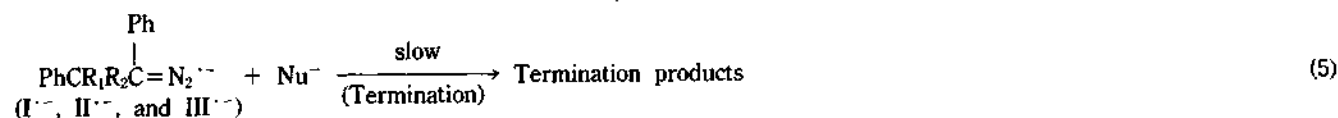
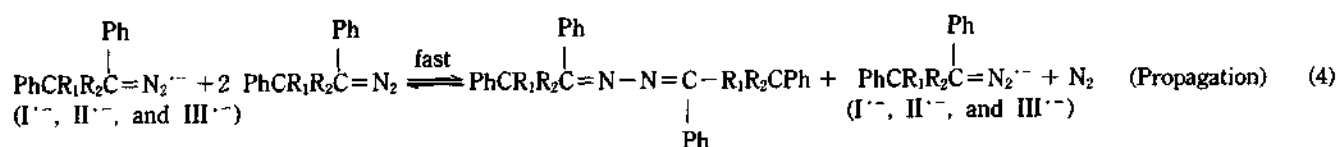
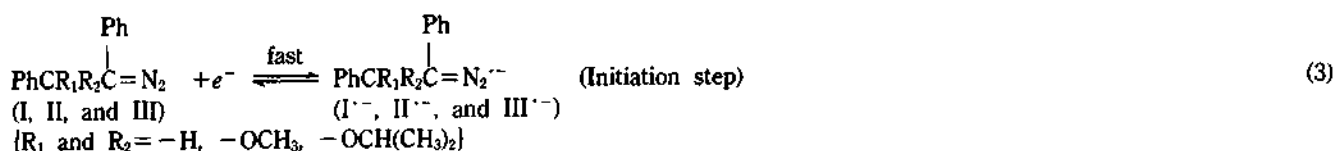
Cyclic Voltammetry. Cyclic voltammeteries were performed in dry acetonitrile containing R₄NBF₄ (R=Me, Et and Bu) in a thermostated glass vessel containing a platinum or gold working electrode, an auxiliary stainless steel electrode, and a reference electrode, Ag/AgNO₃ (0.01 M) or a saturated calomel electrode (SCE) in acetonitrile. The concentration of diazo compound was approximately 5.0×10^{-3} M. The response of current was recorded on a Houston Series 2000 X-Y recorder and a Philips 3233 Oscilloscope.

Kinetic Treatment. The electrolysis was treated as the chemical reactions taking place in homogeneous solution. The electrolyses were interrupted after passage of about 2.5×10^{-4} Faraday. Decompositions of diazo compounds (I, II, and III) were observed as shown in Eq. (3), (4) and (5).

The alkoxy aryldiazo anion radicals (I⁻, II⁻, and III⁻) were observed to be a chain carrier involved in the rate limiting step. The rate constant of initiation step (3), k_i is given by (6) from Nicholson's method⁹. Where i is the constant current and V is the volume of solution in the cathode compartment.

$$k_i = i/FV \quad (6)$$

A modified time variable (τ) is defined as $\tau = t - t_i$ and t_i is the time at which the current is interrupted by passage of about 2.5×10^{-4} F. τ is a predetermined period of time after reduction within the range of $0.01 s \leq \tau \leq 5 s$. The dependence of diazo compound concentration against τ for the case of first-order behavior is given by (7) in the propagation step (4).



$$\ln \frac{[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t}{[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_\infty} = k_1' [\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t (1 - e^{-k_1' t}) \quad (7)$$

Where k_1' is the rate constant of first-order reaction in Nicholson's equation⁹. And the final step for diazo compound concentration is then given by (8) as τ becomes large.

$$\ln \frac{[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t}{[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_\infty} = k_1' [\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t \quad (8)$$

Where k_1' can be obtained from the combination (7) and (8) and from the method which has already been known⁹. Eq. (9) was obtained from the result of combination (7) and (8).

$$\ln \left[1 - \frac{\{\ln[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t / [\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_\infty\}}{\{\ln[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t / [\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_\infty\}} \right] = -k_1' \tau \quad (9)$$

For the first order rate, in termination step $[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t$ is given by (10). Where $[\text{Nu}^-]$ is in excess compared with $[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t$.

$$[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t = \frac{k_t}{k_i} (1 - e^{-k_1' t}) \quad (10)$$

Thus the line of constant current electrolysis experiment was calculated according to (11)

$$\ln \frac{[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_t}{[\text{PhCR}_1\text{R}_2(\text{Ph})\text{C}=\text{N}_2]_\infty} = -k_1' k_i \left[t - \frac{1}{k_1'} (1 - e^{-k_1' t}) \right] \quad (11)$$

Results and Discussion

Kinetic Behavior of the Reactions of Alkoxy-Aryl Diazo Anion Radicals. The cyclic voltammetric reduction of diazo compounds (I, II, and III) was examined at a platinum electrode as a function of temperature ($-5^\circ\text{C} \leq t \leq 30^\circ\text{C}$), scan rate of $0.2\text{--}100 \text{ V}\cdot\text{s}^{-1}$, and supporting electrolyte (R_4NBF_4 , where $\text{R}=\text{Me, Et, Bu}$) in various solvents. Figure 1 shows a cyclic voltammogram for the reduction of I in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ at 298 K, 268 K, and 293 K. The peaks on the return scan represent the oxidation of carbene anion radical. However, at a lower scan rate and low temperature the oxidation peaks have not observed.

The k_1' values in Eq. (8) and (11) can be calculated from the final concentration of diazo compound when τ becomes large. There were some deviations in the rate constants (k_1') probably due to leakages of atmospheric oxygen during the long reaction period. For this reason, a rather low value for k_1' was chosen for further calculations, even though the final concentration of diazo compounds (I, II, and III) were not determined precisely in experiments with low k_1' value. Attempts to fit the kinetic results of the constant current electrolysis experiments to the second-order reaction behavior on the assumption that the termination process would be second-order, were not agreed.

The first-order rate constants in Table 1 were calculated from the derivative cyclic voltammogram and the double potential step chronoamperometry¹⁰ for the reduction of alkoxy-aryl diazo compounds (I, II, and III). In the Eq. (11) k_1' and k_i can be derived from the double potential step chronoam-

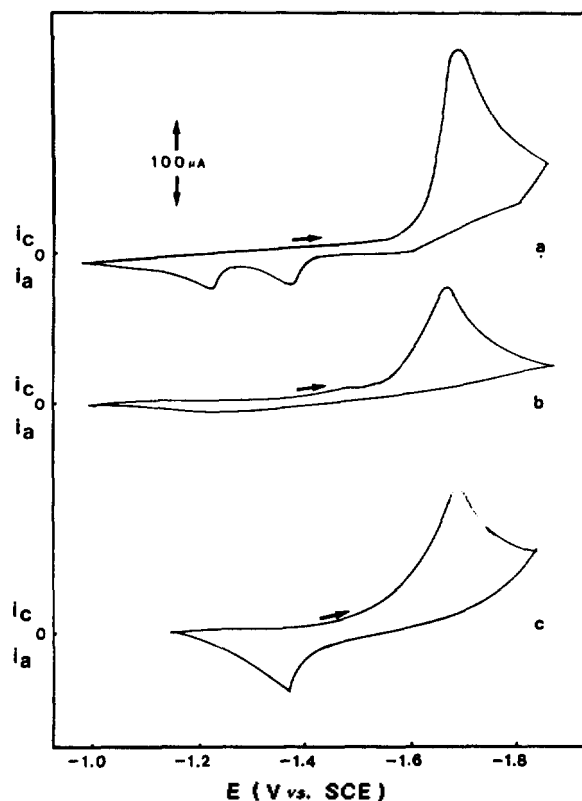


Figure 1. Cyclic voltammogram for the reduction of 2-methoxy-1,2-diphenyl diazoethane (I, 1.0 mM) in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ (1.0 M) at a spherical platinum electrode; (a) $v=50 \text{ V}\cdot\text{s}^{-1}$, $T=298 \text{ K}$; (b) $v=200 \text{ mV}\cdot\text{s}^{-1}$, $T=268 \text{ K}$; (c) $v=80 \text{ V}\cdot\text{s}^{-1}$, $T=293 \text{ K}$ respectively.

Table 1. Rate Constants ($k_1' \times 10^{-2} \text{ s}^{-1}$) for the Reactions of Alkoxy-Aryldiazo Radicals in Various Solutions by Double Potential Step Chronoamperometry at 268 K

Substrates	I ⁻	II ⁻	III ⁻
Electrolytes/Solvents			
$\text{Me}_4\text{NBF}_4/\text{MeCN}$	4.73	3.64	6.27
$\text{Me}_4\text{NBF}_4/\text{DMSO}$	3.12	1.93	3.98
$\text{Me}_4\text{NBF}_4/\text{DMA}$	4.26	3.11	5.83
$\text{Et}_4\text{NBF}_4/\text{MeCN}$	2.92	2.18	3.87
$\text{Et}_4\text{NBF}_4/\text{DMSO}$	2.10	1.46	2.72
$\text{Et}_4\text{NBF}_4/\text{DMA}$	2.74	1.94	3.56
$\text{Bu}_4\text{NBF}_4/\text{MeCN}$	1.99	1.42	2.68
$\text{Bu}_4\text{NBF}_4/\text{DMSO}$	0.954	0.457	2.51
$\text{Bu}_4\text{NBF}_4/\text{DMA}$	1.83	1.24	2.35

perometric technique¹⁰. The applied potential (E_f) for forward reaction in the double potential step chronoamperometry was constant during the reaction ($t > 0$) and the step component which is the difference between the applied potential for backward reaction (E_b) and E_f was also constant. $E_b - E_f$ was superimposed on the constant perturbation for $t > \tau$.

The reactions of alkoxy-aryl diazo anion radical in this study have been shown to involve stepping in the forward

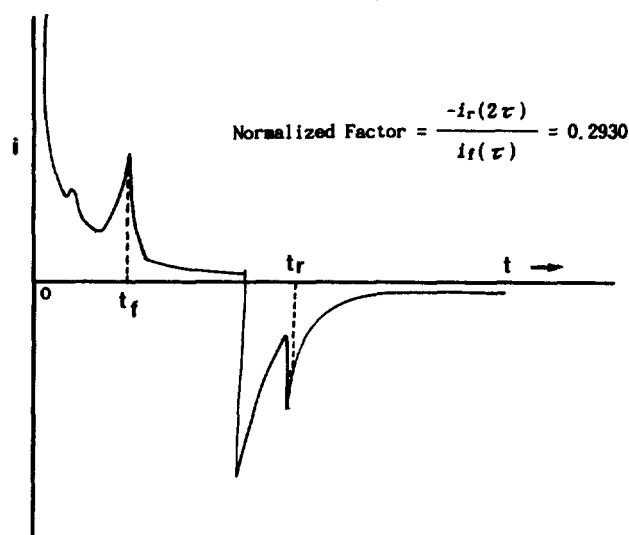


Figure 2. The current response against the time scale (t) for the reduction of 2-methoxy-1,2-diphenyl diazoethane (I) in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ solution in double-step chronoamperometry (observed $\tau=5.18$ ms).

phase to the potential on the diffusion plateau of the reaction wave, then reversing to a potential on the diffusion plateau for reoxidation at higher temperatures. The current-time curves can be obtained from the Kambara's Eq. (12)¹⁰.

$$-i_r(t) = \frac{nFAD_0^{1/2}C_0^*}{\pi^{1/2}} \left[\frac{1}{(t-\tau)^{1/2}} - \frac{1}{t^{1/2}} \right] \quad (12)$$

Where D_0 is the diffusion coefficient and A is the area which is given by Fick's law of diffusion¹¹. C_0^* is the concentration which reaches a constant value by the semi-infinite boundary conditions¹⁰. The ratio of the reversal current (i_r) to the forward current (i_f) was given by (13)¹⁰ modified from (12).

$$\frac{-i_r}{i_f} = \left(\frac{t_f}{t_r - \tau} \right)^{1/2} - \left(\frac{t_f}{t_r} \right)^{1/2} \quad (13)$$

t_r and t_f were determined as $t_r - \tau = t_f$ on the assuming that the currents are proportional to $AD_0^{1/2}$, then

$$\frac{-i_r}{i_f} = 1 - \left[1 - \frac{\tau}{t_r} \right]^{1/2} \quad (14)$$

The ratio of the reversal current to the forward current was normalized as $-i_r(2\tau)/i_f(\tau)=0.2930$. The current responses for the reduction of I in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ solution in double-step chronoamperometry was shown in Figure 2.

The calculated value for $t^{1/2} \cdot i_f$ is 1.010 when the normalized factor is 0.2930 for the reduction of I in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ solution in double-step chronoamperometry. The values of $t^{1/2} \cdot i_f$ have been widely used to interpret electrochemical mechanisms^{4,10,12}.

In the case of the heterogeneous electron transfer followed by a homogeneous chemical reaction (EC mechanism) the value of $t^{1/2} \cdot i_f$ is shown to be 1.000 when the normalized factor is 0.5000¹². While the value of $t^{1/2} \cdot i_f$ is shown to be from 0.935 to 1.150 as the values are very dispersed in a wide range¹⁴ in the case of the overall two electron process with a homogeneous electron transfer following the rate-de-

Table 2. Double Potential Step Chronoamperometry Data for the Reaction of Alkoxy-Aryldiazo Radicals in Various Solvents at 268 K

	I ⁻		II ⁻		III ⁻	
	$-i_r(2\tau)/i_f(\tau)$	$t^{1/2} \cdot i_f$	$-i_r(2\tau)/i_f(\tau)$	$t^{1/2} \cdot i_f$	$-i_r(2\tau)/i_f(\tau)$	$t^{1/2} \cdot i_f$
$\text{Me}_4\text{NBF}_4/\text{MeCN}$	0.2930	1.010	0.2931	1.011	0.2928	1.011
	0.5000	1.007	0.5004	1.003	0.5002	1.004
$\text{Me}_4\text{NBF}_4/\text{DMSO}$	0.2932	1.011	0.2930	1.010	0.2931	1.010
	0.5000	1.005	0.5001	1.006	0.4997	1.003
$\text{Me}_4\text{NBF}_4/\text{DMA}$	0.2931	1.011	0.2930	1.009	0.2929	1.009
	0.5000	1.004	0.5003	1.007	0.5003	1.002
$\text{Et}_4\text{NBF}_4/\text{MeCN}$	0.2929	1.010	0.2933	1.010	0.2930	1.011
	0.5000	1.006	0.5000	1.004	0.5001	1.005
$\text{Et}_4\text{NBF}_4/\text{DMSO}$	0.2928	1.000	0.2929	1.012	0.2932	1.010
	0.5002	1.004	0.5002	1.004	0.5005	1.002
$\text{Et}_4\text{NBF}_4/\text{DMA}$	0.2931	1.011	0.2930	1.008	0.2931	1.008
	0.5004	1.008	0.4998	1.007	0.5004	1.002
$\text{Bu}_4\text{NBF}_4/\text{MeCN}$	0.2930	1.016	0.2932	1.012	0.2930	1.009
	0.5001	1.003	0.5001	1.008	0.5002	1.004
$\text{Bu}_4\text{NBF}_4/\text{DMSO}$	0.2932	1.012	0.2928	1.013	0.2928	1.010
	0.5005	1.007	0.5000	1.009	0.4998	1.007
$\text{Bu}_4\text{NBF}_4/\text{DMA}$	0.2933	1.018	0.2931	1.011	0.2932	1.009
	0.5011	1.009	0.5003	1.005	0.5003	1.003

termining step (ECE mechanism) when the normalized factor is 0.5000¹². In this study the calculated factor is equal to 0.2930 and the value of $t^{1/2} \cdot i_f$ is equal to 1.010 for the reduction of I in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ solution. Therefore the data do give an approximate value to approach the EC mechanism rather than the ECE mechanism.

The EC mechanism is favored for the reduction of I in $\text{Me}_4\text{NBF}_4/\text{MeCN}$ solution so that I in Eq. (3) could be an electroactive species and I⁻ in Eq. (3) must be reacted to produce a species that is not electroactive at potentials where the reduction of I is occurring by the criterion of EC reaction mechanism¹⁵.

Other data which were obtained from II and III in all solutions by the double potential step chronoamperometry were satisfied the EC mechanism as shown in Table 2. In order to investigate the EC mechanism more accurately the double potential step chronoamperometry was performed at the value of 0.5000 approximately at the normalized factor $[-i_r(2\tau)/i_f(\tau)]$ in Table 2.

At the two normalized factors of the region of 0.2930 and 0.5000 approximately the values of $t^{1/2} \cdot i_f$ showed nearly unit, in consequence, the data revealed to fit the EC mechanism. Therefore, the rate constants were calculated from the criterion of EC mechanism and summarized in Table 1.

The rate constants of the reactions of alkoxy-aryl diazo radicals in various solutions by double potential step chronoamperometry are in the order as III⁻ > I⁻ > II⁻ as shown in Table 1. It seems that III⁻ promotes effectively the formation of the carbene anion radical in the termination step Eq. (5) more than I⁻ and II⁻. The effect of dipolar aprotic

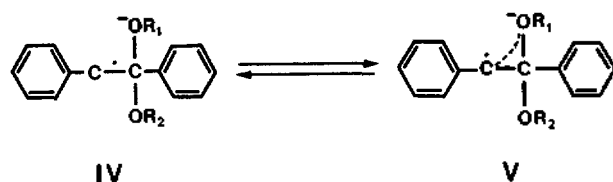
Table 3. The Voltage Sweep Rate ($v_{1/2}/Vs^{-1}$) Data for Decomposition of Alkoxy-Aryldiazo Radicals in Acetonitrile at 268 K

[H ₂ O], M	I ^{-•}	II ^{-•}	III ^{-•}
	($v_{1/2}/Vs^{-1}$) _{H₂O}	($v_{1/2}/Vs^{-1}$) _{H₂O}	($v_{1/2}/Vs^{-1}$) _{H₂O}
0	78.9	60.6	104
0.0520	80.2	63.8	112
0.104	94.8	75.4	132
0.208	131	104	182
0.416	198	157	275
0.624	303	240	420

solvents has been decreased the order, MeCN>DMA>DMSO as shown in Table 1. This indicates that the reaction was deactivated with increasing the dielectric constant of the solvent. This means that the solvent having high dielectric constant restrains the EC mechanism since the solvent acts as a hindrance to the electrode reaction so that the formation of anion radical in the termination step is delayed by the solvent of higher value of dielectric constant.

Decomposition Mechanism of Alkoxy-Aryl Diazo Anion Radicals. Table 1 shows that the reductions of I, II and III in various solutions are consistent with the mechanism of unimolecular loss of dinitrogen from I^{-•}, II^{-•}, and III^{-•} to give the corresponding carbene anion radical. Because the kinetic results can be secured evidence supporting that the anion radicals of I^{-•}, II^{-•}, and III^{-•} have shown to be sufficiently long-lived radicals by EC mechanism.

In the second step, a species of PhCR₁R₂(Ph)C=N-N=C(Ph)R₃R₄CPh is nonelectroactive and I^{-•}, II^{-•}, and III^{-•} react with the nucleophiles to produce a species that is not electroactive at potential in the final step. It is believed that the carbene anion radical was produced by the reaction of unimolecular loss of nitrogen from I^{-•}, II^{-•}, and III^{-•} and the structure for formation of carbene anion radical shows to be a resonance structure (IV and V).



Effect of Nucleophiles. The nucleophiles contribute to terminate propagation step, Eq. (4) and to produce the products, Eq. (5). To test the nucleophilic termination, the voltage sweep rate, $v_{1/2}$ was measured as a function of the added water concentration in MeCN. A good linear relationship between the rate constants of the EC mechanism and the values of $v_{1/2}$. The values of $v_{1/2}$ were measured for the normalized factor to equal 0.5000 and the other results were shown in Table 3.

As shown in Table 3, the decomposition rate of alkoxy aryl diazo anion radicals is accelerated on increasing in water concentration more than the dipolar aprotic solvent effect or the effect of quaternary ammonium ions of the supporting electrolyte. This results assumes that the anion radicals I^{-•}, II^{-•}, and III^{-•} react with water molecule stronger than neutral diazo compounds (I, II, and III). Therefore, the anion radicals in the termination step might be involved in the bond breaking of the hydrogen bond between water molecule and aprotic solvent molecule. The disappearance of the negative charge of the anion radical after the hydrogen bond cleavage between water and the dipolar aprotic solvent such as MeCN may contribute to increase the rate of dinitrogen since the intermediate would have increased the neutral radical character.

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