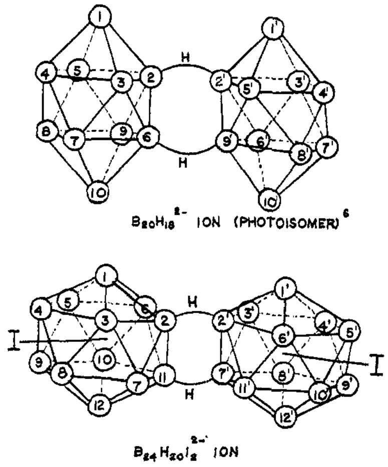

Figure 1. Circles represent boron atoms. Each boron of $B_{20}H_{18}^{2-}$ except 2,6,2′,9′ is bonded to a terminal H. Each boron in the proposed structure of $B_{24}H_{20}I_2^{2-}$ except 2,11,2′,7′ is bonded to a terminal H or I.

A sample of $[(C_2H_5)_4N]_3B_{24}H_{21}I_2$ (2.44 g, 2.64 mmol) was dissolved in 50 ml of acetonitrile (0.1 *M* tetraethylammonium perchlorate as supporting electrolyte). The solution was exhaustively electrolyzed under nitrogen at +1.3 V (sce), using a graphite cloth electrode. The current was monitored and corresponded to the value $n = 2.04$ equiv per mol of $[(C_2H_5)_4N]_3B_{24}H_{21}I_2$. The electrolyzed solution was added to 400 ml of H_2O and titrated with standardized NaOH solution. The titration indicated that 0.92 mol of H^+ per mol of $B_{24}H_{21}I_2^{3-}$ was formed in the oxidation process. The aqueous solution was heated to boiling to remove the acetonitrile. The precipitate which formed as the acetonitrile evaporated was collected by filtration of the hot solution and recrystallized from an acetonitrile–water mixture. Almost quantitative yields of the product were obtained by this procedure. *Anal.* Calcd for $[(C_2H_5)_4N]_2B_{24}H_{20}I_2$: B, 32.68; I, 31.97; equiv wt, 398.0. Found: B, 31.0; I, 31.6; equiv wt, 400. The ir spectrum included absorptions at 2510 and 2200 cm^{-1}. The 32-MHz ^{11}B nmr spectrum of $[(C_2H_5)_4N]_2B_{24}H_{20}I_2$ in acetonitrile consisted of a single poorly resolved doublet 34.1 ppm upfield from external methyl borate. The ^1H nmr spectrum of aqueous $Na_2B_{24}H_{20}I_2$ with ^{11}B decoupled consisted of at least three signals at 1.17, 1.30, and 1.55 ppm downfield from internal sodium 3-(trimethylsilyl)-1-propanesulfonate. Only end absorption was observed near 200 nm in the uv spectrum.

A one-electron oxidation of $B_{10}H_{10}^{2-}$ yields either $B_{20}H_{19}^{3-}$ or $B_{20}H_{18}^{4-}$, depending on the pH of the medium. Under slightly more vigorous conditions, a higher oxidation state results, $B_{20}H_{18}^{2-}$.[4] In $B_{20}H_{18}^{4-}$, there is a direct B–B bond between B_{10} cages, and that bond is apparently protonated to form a BHB bridge bond in $B_{20}H_{19}^{3-}$.[4b,c] In the higher oxidation state, $B_{20}H_{18}^{2-}$, two B_{10} cages are linked by a pair of BBB three-center bonds.[4b,5] Uv irradiation of $B_{20}H_{18}^{2-}$ gives a photoisomer in which two B_{10} cages are linked by a pair of BHB bridge bonds.[6] The $B_{24}H_{23}^{3-}$ ion is analogous to $B_{20}H_{19}^{3-}$, and the new $B_{24}H_{20}I_2^{2-}$ should be analogous to $B_{20}H_{18}^{2-}$.

The transfer of two electrons and liberation of one H^+ per $B_{24}H_{21}I_2^{3-}$ support this analogy (eq 1). The equivalent weight and analyses for boron and iodine lead to

$$B_{24}H_{21}I_2^{3-} \longrightarrow B_{24}H_{20}I_2^{2-} + H^+ + 2e^- \tag{1}$$

the formulation $B_{24}H_{20}I_2^{2-}$. The lack of a uv absorption maximum (observed for the stable isomer of $B_{20}H_{18}^{2-}$ and not for the photoisomer) and the presence of an ir band at 2200 cm^{-1} (BHB bridge, absent in the stable isomer of $B_{20}H_{18}^{2-}$ and present in the photoisomer) suggest a structure for $B_{24}H_{20}I_2^{2-}$ analogous to that of the photoisomer of $B_{20}H_{18}^{2-}$ (see Figure 1). Unfortunately, the nmr spectra do not provide an unambiguous indication of the structure of the $B_{24}H_{20}I_2^{2-}$ ion. The presence of at least three environments in the ^1H nmr spectrum and a poorly resolved doublet in the ^{11}B nmr spectrum indicate either that the oxidized ion is a mixture of isomers with respect to the iodine substituents due to a lack of stereospecificity in the reactions, or that the positions of the iodine atoms lower the symmetry of the ion to the point that no unique structure can be assigned on the basis of the spectral data. Models based on the stable isomer of $B_{20}H_{18}^{2-}$ suggest that H-H repulsions between cages will be more severe for coupled B_{12} cages than for coupled B_{10} cages. These steric repulsions can be significantly reduced by the formation of BHB bridge bonds between cages instead of direct BB or BBB bonds.

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(4) (a) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **48**, 729 (1962); (b) B. L. Chamberland and E. L. Muetterties, *Inorg. Chem.*, **3**, 1450 (1964); (c) M. F. Hawthorne, R. L. Pilling, and P. F. Stokely, *J. Amer. Chem. Soc.*, **87**, 1893 (1965); (d) R. L. Middaugh and F. Farha, Jr., *ibid.*, **88**, 4147 (1966).

(5) C. H. Schwalbe and W. N. Lipscomb, *ibid.*, **91**, 194 (1969).

(6) (a) M. F. Hawthorne and R. L. Pilling, *ibid.*, **88**, 3873 (1966); (b) B. G. Deboer, Z. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **7**, 1085 (1968).

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Evaluation of Fast Homogeneous Electron-Exchange Reaction Rates Using Electrochemistry and Reflection Spectroscopy

Sir:

We wish to report the evaluation of the kinetic rates of fast homogeneous reactions involving electrogenerated species using the technique of internal reflection spectroscopy (irs) at optically transparent electrodes (ote). This technique has not been previously applied successfully to kinetic measurements. Moreover, we wish to demonstrate that fast homogeneous rates approaching diffusional control are determinable, taking advantage of the repetitiveness of the process for improvement of the signal to noise ratio.

Although this technique can be applied in general to follow any species whose concentration is perturbed through a heterogeneous electrochemical reaction, the reaction scheme[1,2]

$$A \longrightarrow B \pm e^- \qquad E_1^0 \tag{1}$$

$$B \longrightarrow C \pm e^- \qquad E_2^0 \tag{2}$$

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(1) J. W. Strojek, T. Kuwana, and S. W. Feldberg, *J. Amer. Chem. Soc.*, **90**, 1353 (1968).

(2) T. Kuwana and J. W. Strojek, *Discuss. Faraday Soc.*, **45**, 134 (1968).

with the equilibrium reaction

$$\mathrm{A} + \mathrm{C} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} 2\mathrm{B} \qquad (3)$$

where k_f and k_b are the rate constants of the forward and reverse reactions in the equilibrium, will be used as an example. The redox potentials, E_1^0 and E_2^0, and the equilibrium constant for reaction 3, $K_{eq} = k_f/k_b$, are thermodynamically related[2] as previously discussed for the normal transmission spectral studies. Experimentally, the approach is to follow the irs absorbance of either reactant or products during the usual potential step (chronoamperometric) experiment where the concentration at the electrode surface is zero. Thus, mechanistically, species A is transformed at the electrode at a diffusion-controlled rate; as C moves to the bulk solution by diffusion, it encounters A diffusing toward the electrode and reaction occurs to attain equilibrium.

Theoretical analysis of this problem is similar to previously discussed work[3] with the exception that the "optical cell" is now restricted and defined by the penetration depth δ of the light beam into the solution phase. The *initial requirement* is to mathematically analyze and experimentally verify the light absorbance A as a function of time for the simplest case, *i.e.*, reaction 1, for a chronoamperometric experiment where the rate of electrochemical transformation is controlled by diffusion. The relation to solve is

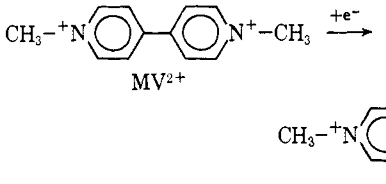
$$A(t) = N_{\text{eff}}\epsilon \int_0^\infty C(x,t) \exp(-x/\delta) \mathrm{d}x \qquad (4)$$

where N_{eff} is a sensitivity factor characteristic of the ote and number of reflections, ϵ is the molar extinction coefficient of the monitored species, and $C(x,t)$ is the concentration of the same species. The solution of eq 4 for species B through Laplace analysis gives

$$A_B(t) = N_{\text{eff}}\epsilon_B\delta C_A{}^0\{1 - \exp(a^2t) \operatorname{erfc}(\sqrt{t})\} \qquad (5)$$

where $a = \sqrt{D}/\delta$.

The calculated and experimental A *vs.* t curves are shown in Figure 1, curves a and c, for the one-electron reduction of methyl viologen to the monocation radical



MV^{2+} MV^{+} (6)

and the oxidation of $Ta_6Br_{12}{}^{2+}$ cluster to the 3+ species,[4] respectively. Agreement with predicted results is within 5% at 50 μsec. The experimental curve is an output from a PAR Waveform Eductor which signal averages the repetitive A *vs.* t curve. The repetition is possible in irs since the optical cell can be "filled" and "dumped" at will by controlling the value and width of the potential pulses. This advantage allows the resolution of small absorbance changes on a time scale heretofore unattainable.

Any homogeneous chemical reaction, which perturbs the concentration of the optically monitored species, alters the A *vs.* t curve from the diffusion-controlled case, as long as this reaction is sufficiently fast such that it occurs within the optical cell defined by δ. For the disproportionation reaction 3 as dictated by the experimental conditions, a working curve for the irs absorbance can be computed by a digital simulation of the concentration profile.[5] Experimentally MV^{2+} undergoes two consecutive one-electron transfers with $E_1{}^{0\prime}$ and $E_2{}^{0\prime}$ of -0.50 and -0.92 V *vs.* sce in acetonitrile.[6,7] To evaluate the k_f of this reaction, the potential is stepped about 200 mV more negative than $E_2{}^{0\prime}$ so that the transformation of MV^{2+} to MV^0 occurs at the electrode at a diffusion-controlled rate. The absorbance of MV$\cdot^+$ is monitored during the potential step as shown in Figure 1, curve b, and k_f is evaluated from matching the observed absorbance to the working curve. Similarly, in the case of $Ta_6Br_{12}{}^{2+}$ two oxidation waves of one electron each are observed with $E_1{}^{0\prime}$ and $E_2{}^{0\prime}$ of 0.35 and 0.65 V *vs.* sce.[8] The $Ta_6Br_{12}{}^{2+}$ was monitored during potential step, Figure 1, curve d, and the k_f for the reaction was evaluated from the working curve.

$$Ta_6Br_{12}{}^{2+} + Ta_6Br_{12}{}^{4+} \underset{}{\overset{k_f}{\rightleftharpoons}} 2Ta_6Br_{12}{}^{3+} \qquad (7)$$

The data for $Ta_6B_{12}{}^{2+}$ are summarized in Table I for two different concentrations.

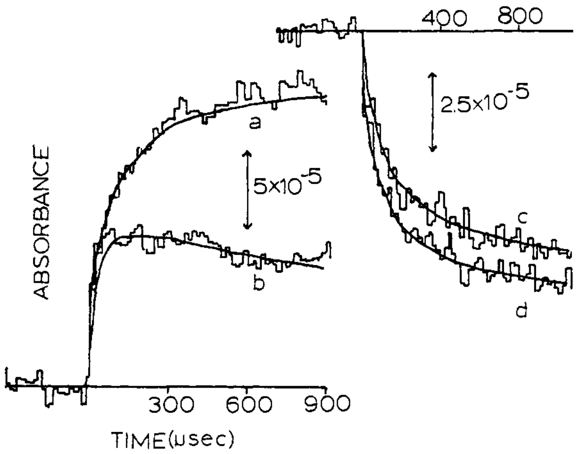


Figure 1. A *vs.* t behavior for MV^{2+} reduction and $Ta_6Br_{12}{}^{2+}$ oxidation. Curve a, potential stepped beyond $E_1{}^{0\prime}$ and curve b, beyond $E_2{}^{0\prime}$ for MV$\cdot^+$ at λ 605 mμ, $\epsilon = 2 \times 10^4$ M^{-1} cm^{-1} in 0.5 M tetraethylammonium perchlorate in acetonitrile. Solid line drawn for $C^0 = 2.5 \times 10^{-4}$ M, $K_{eq} = 10^7$, $\sqrt{D}/\delta = 98.6$ sec$^{-1/2}$, $k_f \geqslant 3 \times 10^9$ M^{-1} sec^{-1}. Curve c, potential stepped beyond $E_1{}^{0\prime}$, and curve d, beyond $E_2{}^{0\prime}$ for $Ta_6Br_{12}{}^{2+}$ for conditions given in Table I. Solid line drawn for $C_A{}^0 = 2.7 \times 10^{-4}$ M, $\sqrt{D}/\delta = 58$ sec$^{-1/2}$, $k_f = 6.9 \times 10^7$ M^{-1}. All scans were obtained by applying 2-msec potential pulse with repetition rate of 50 Hz for 60 sec; $t = 25 \pm 1°$.

The value of 3×10^9 M^{-1} sec^{-1} for the methyl viologen electron exchange between the neutral and divalent cation represents the upper limit attainable with the present experimental ote cell and instrumentation. Limitations are due to the finite resistance of the ote and large power level required for the potentiostat at times less than 10 μsec. Irs at ote taking advantage of the repetition of the process allows monitoring of

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(3) N. Winograd and T. Kuwana, *J. Electroanal. Chem.*, **23**, 333 (1969).

(4) J. H. Espenson, *Inorg. Chem.*, **7**, 631 (1968).

(5) S. W. Feldberg in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker Inc., New York, N. Y., 1969.

(6) J. W. Strojek, G. A. Gruver, and T. Kuwana, *Anal. Chem.*, **41**, 481 (1969).

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(8) N. E. Cooke, J. H. Espenson, and T. Kuwana, to be published.

Table I. Kinetic Data for $Ta_6Br_{12}^{2+}$

t, μsec	$A \times 10^5$ [a]	$kC_A^{\circ}t$ [b]	Log k_f, M^{-1} sec^{-1}
(A) $C_A^0 = 1.0 \times 10^{-4}\ M$; $\sqrt{D}/\delta^c = 77.2$ sec$^{-1/2}$; $N_{eff} = 9.7$			
168	7.40	0.93	7.71
378	4.82	1.95	7.72
671	2.86	5.10	7.88
1048	1.73	9.5	7.94
1306	1.35	10.0	7.88
			Av = 7.83 ± 0.10
(B) $C_A^0 = 2.7 \times 10^{-4}\ M$; $\sqrt{D}/\delta = 98$ sec$^{-1/2}$; $N_{eff} = 7.0$			
297	5.46	6.6	7.91
669	3.08	12.5	7.84
1189	1.62	24.6	7.87
1858	1.08	27.0	7.76
			Av = 7.84 ± 0.06

[a] $Ta_6Br_{12}^{2+}$ monitored at 620 mμ, where $\epsilon \approx 6000\ M^{-1}\ cm^{-1}$, $K_{eq} = 1 \times 10^5$. [b] Kinetic data evaluated from potential step beyond $E_2^{0\prime}$, 0.04 M $HClO_4$ used as supporting electrolyte. [c] $\sqrt{D}/\delta$ evaluated from potential step beyond $E_1^{0\prime}$.

any light-absorbing species within the confines of the irs optical cell during an electrochemical perturbation. High sensitivity, due to $N_{eff} \gg 1$, and signal averaging give absorbance sensitivity better than one part in 10^5 with time resolution in the microsecond range. Detailed mechanism and kinetic studies of fast homogeneous electron exchange reactions following the heterogeneous electron-transfer step at ote are now in progress.

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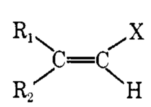
Modification of the Wittig Reaction to Permit the Stereospecific Synthesis of Certain Trisubstituted Olefins. Stereospecific Synthesis of α-Santalol

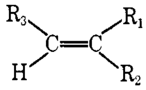
Sir:

It has been shown[1] that the reaction between an aldehyde and an alkylidenetriphenylphosphorane to form a 1,2-disubstituted ethylene can be directed efficiently to the *trans* isomer by interposing a process which modifies the stereochemistry of the intermediate phosphorus betaine. The process which was described involves sequential treatment of the primary betaine (resulting from addition of the Wittig reagent to the aldehyde) with phenyllithium (at −70°) and potassium *t*-butoxide–*t*-butyl alcohol. Experiments performed in these laboratories indicated that, at least in the cases studied, the potassium *t*-butoxide–*t*-butyl alcohol reagent is *not required* for the Wittig–Schlosser synthesis.[2] This finding implied that the intermediate β-oxido phosphonium ylide (the obvious product of the reaction of a phosphorus betaine with phenyllithium) is capable of stereospecific protonation to form the *threo* betaine which is the precursor of the *trans*-1,2-disubstituted ethylene finally formed. It seemed logical to expect that only one of the isomeric betaines might be formed specifically by the reaction of electrophiles other than proton donors with β-oxido phosphonium ylides and that a useful stereospecific route to trisubstituted olefins might thereby become available. This communication describes the realization of such a synthetic process.[3] Publication of the results which have been obtained thus far is prompted by the appearance of a note describing a study of reactions of β-oxide phosphonium ylides[4] which partially overlaps the present work.

Methods which have been described previously permit the stereospecific synthesis of trisubstituted olefins of types **1a**,[3,5] **1b**,[3,5] and also **2a**,[3a,6] but not of type **2b**. We shall first describe a new approach to the synthesis of



1a, $R_1 = CH_3$; R_2 = alkyl
1b, R_1 = alkyl; $R_2 = CH_3$
($X = CH_2OH$ or $COOCH_3$)



2a, $R_1 = CH_3$; R_3 = alkyl; $R_2 = CH_2OH$ or $COOCH_3$
2b, $R_1 = CH_2OH$ or $COOCH_3$; $R_2 = CH_3$; R_3 = alkyl

olefins of type **2b**, *via* β-oxido phosphonium ylides as key intermediates, which closes this methodological gap. Reaction of a solution of ethylidenetriphenylphosphorane in tetrahydrofuran at −78° with heptanal for 5 min produced the betaine **3** which was treated with 1 equiv of *n*-butyllithium (in hexane) at −78° to form the deep red β-oxido phosphonium ylide **4**. The solution of the relatively stable ylide **4** was allowed to warm to 0° and then treated with 2 equiv of dry paraformaldehyde to generate the colorless β,β′-dioxido phosphonium derivative **5**. After a reaction time of 0.5 hr at 0° and 12 hr at 25°, the mixture was worked up in the usual way to give 2-methyl-*cis*-2-nonen-1-ol (6) in 73% yield. The stereochemistry of 6 is clearly indicated by analysis[7–9] of the nmr spectrum (in CCl_4) which

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[1] M. Schlosser and K. F. Christmann, *Angew. Chem. Intern. Ed. Engl.*, **5**, 126 (1966); *Ann. Chem.*, **708**, 1 (1967).

(2) We suggest this name for the modified[1] Wittig reactions which afford *trans*-1,2-disubstituted olefins.

(3) For other recent contributions from this laboratory on new stereospecific routes to trisubstituted olefins, see (a) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 4245 (1967); (b) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *ibid.*, **90**, 5618 (1968); (c) E. J. Corey and J. A. Katzenellenbogen, *ibid.*, **91**, 1851 (1969).

(4) M. Schlosser and K. F. Christmann, *Synthesis*, **1**, 38 (1969), describe the reaction of certain β-oxido ylides with methyl iodide, perchloryl fluoride, iodobenzene dichloride, and bromine.

(5) E. J. Dorey, N. W. Gilman, and B. C. Ganem, *J. Amer. Chem. Soc.*, **90**, 5616 (1968).

(6) E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *ibid.*, **91**, 4318 (1969).

(7) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, **33**, 3382 (1968).