

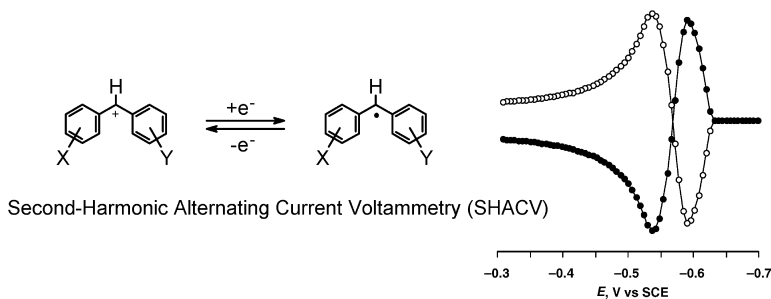
Article

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## Role of Electron-Transfer Processes in Reactions of Diarylcarbenium Ions and Related Quinone Methides with Nucleophiles

Armin R. Ofial,<sup>†</sup> Kei Ohkubo,<sup>‡</sup> Shunichi Fukuzumi,<sup>\*,‡</sup> Roland Lucius,<sup>†,§</sup> and Herbert Mayr<sup>\*,†</sup>

Contribution from the Department Chemie der Ludwig-Maximilians-Universität München, Butenandtstr. 5-13 (Haus F), D-81377 München, Germany, and Department of Material and Life Science, Graduate School of Engineering, Osaka University, CREST, Japan Science and Technology Corporation (JST), 2-1, Yamada-oka, Suita, Osaka 565-0871, Japan

Received March 17, 2003; E-mail: Herbert.Mayr@cup.uni-muenchen.de; fukuzumi@ap.chem.eng.osaka-u.ac.jp

**Abstract:** Second-harmonic alternating current voltammetry has been used to determine one-electron reduction potentials of 15 diarylcarbenium ions and 5 structurally analogous quinone methides, which have been employed as reference electrophiles for the development of nucleophilicity scales. A linear correlation ( $r^2 = 0.993$ ) between the empirical electrophilicity parameters  $E$  and the reduction potentials in acetonitrile ( $E = 14.091E_{\text{red}}^{\circ} - 0.279$ ) covering a range of 1.64 V (or 158 kJ mol<sup>-1</sup>) has been observed. For a large number of nucleophiles, it has been demonstrated that the observed activation free energies of the electrophile–nucleophile combinations are 61–195 kJ mol<sup>-1</sup> smaller than the free energy change of electron transfer from nucleophile to electrophile, which definitely excludes outer-sphere electron transfer occurring during these reactions.

### Introduction

The empirical electrophilicity parameters  $E$ , as first defined in 1994<sup>1</sup> and standardized in 2001,<sup>2</sup> proved to be extremely useful for quantitatively describing the reactivities of carbocations and related electrophiles<sup>3</sup> with a large variety of  $\pi$ -,  $n$ -, and  $\sigma$ -nucleophiles,<sup>2–7</sup> including alkenes,<sup>2,4</sup> arenes,<sup>2,4</sup> allyl silanes,<sup>2,4</sup> enol ethers,<sup>2,4</sup> ketene acetals,<sup>2,4</sup> enamines,<sup>2,5</sup> hydride donors,<sup>2,7</sup> carbanions,<sup>3</sup> amines,<sup>6</sup> alcohols,<sup>6</sup> and thiolates.<sup>6</sup>

It has been demonstrated that eq 1

$$\log k(20\text{ }^{\circ}\text{C}) = s(N + E) \quad (1)$$

where electrophiles are characterized by one parameter ( $E$ ) and nucleophiles are characterized by the nucleophilicity parameter  $N$  and the slope parameter  $s$  usually predicts rate constants for

the combinations of these electrophiles with nucleophiles with an accuracy better than a factor of 10–100,<sup>2–7</sup> which is quite remarkable in view of the 25 orders of magnitude presently covered by each, the  $E$ - and  $N$ -scale.

Because a single set of reactivity parameters appears to be sufficient for describing reactions as different as Friedel–Crafts alkylations, Tsuji–Troost allylations, Michael additions, and many others,<sup>3</sup> it is a challenge to reveal the physical basis underlying these relationships. Theoretical investigations (DFT calculations) have already analyzed the correlations between the electrophilicities of benzhydrylium ions (= diarylcarbenium ions), which serve as reference electrophiles,<sup>2</sup> with their Lewis acidities<sup>8</sup> (i.e., carbocation “stabilities”) as well as with the global electrophilicity indices according to Parr.<sup>9</sup>

Since in the transition states of the reactions under consideration (eq 2) electrons are partially shifted from nucleophiles to electrophiles,<sup>10</sup> one might expect a correlation between the electrophilicity parameters  $E$  and the corresponding reduction potentials  $E_{\text{red}}^{\circ}$ .<sup>10d,i,n</sup>



In this investigation we determined the one-electron reduction potentials of the benzhydryl cations and the structurally related quinone methides, which have been employed as reference

\* To whom correspondence should be addressed.

<sup>†</sup> Universität München.

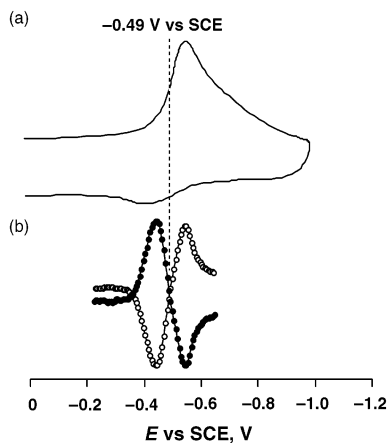
<sup>‡</sup> Osaka University.

<sup>§</sup> Current address: SAP AG, D-69190 Walldorf, Germany.

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**Figure 1.** (a) Cyclic voltammogram (CV) of  $(\text{dma})_2\text{CH}^+\text{BF}_4^-$  in deaerated  $\text{CH}_2\text{Cl}_2$  containing tetrabutylammonium perchlorate (0.1 M) with a gold microelectrode (i.d.  $25\ \mu\text{m}$ ) at 298 K; sweep rate  $100\ \text{V s}^{-1}$ . (b) Second-harmonic AC voltammogram (SHACV) of  $(\text{dma})_2\text{CH}^+\text{BF}_4^-$  in deaerated  $\text{CH}_2\text{Cl}_2$  containing tetrabutylammonium perchlorate (0.1 M) with Au working electrode (i.d. 1.6 mm) and Pt counter electrode; sweep rate  $4\ \text{mV s}^{-1}$ .

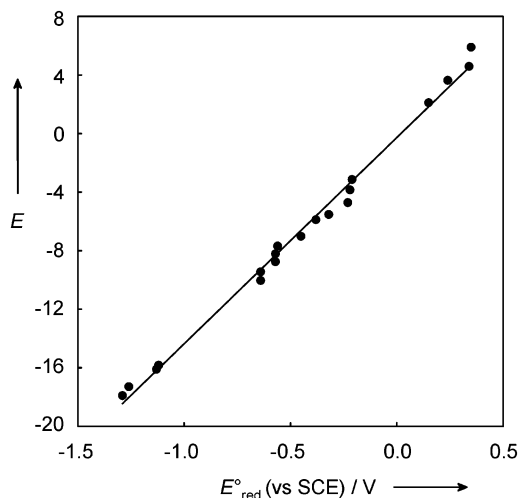
electrophiles, by the second-harmonic alternating current voltammetry (SHACV)<sup>11</sup> method.

### Experimental Section

The fast scanning cyclic voltammetry (CV) and second-harmonic ac voltammetry (SHACV)<sup>11</sup> measurements of benzhydryl cations were carried out with BAS 100B and BAS 100W electrochemical analyzers in deaerated acetonitrile (or dichloromethane) containing 0.10 M  $n\text{-Bu}_4\text{N}^+\text{ClO}_4^-$  (TBAP) as a supporting electrolyte at 298 K (see Figure 1 and the Supporting Information). At a sweep rate of  $100\ \text{V s}^{-1}$ , the CV wave becomes quasi-reversible as shown in Figure 1a, where the anodic wave is smaller than the cathodic wave. The same  $E^\circ_{\text{red}}$  value is obtained by the SHACV measurement (Figure 1b). The gold working electrode (BAS, surface i.d. 1.6 mm) and microelectrode (BAS, surface i.d.  $25\ \mu\text{m}$ ) were polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgNO<sub>3</sub> (0.01 M) reference electrode. The  $E^\circ_{\text{red}}$  values (vs Ag/AgNO<sub>3</sub>) are converted into those vs SCE by addition of 0.29 V.<sup>12</sup>

### Results and Discussion

Previous kinetic investigations have shown that the reactivity range of the benzhydrylium ions and quinone methides used as



**Figure 2.** Correlation of the empirical electrophilicity parameters  $E$  with the one-electron reduction potentials  $E^\circ_{\text{red}}$  (vs SCE, AN, 298 K) of benzhydrylium ions and structurally analogous quinone methides.

reference electrophiles covers 24 orders of magnitude corresponding to reaction times of 1 s vs  $10^{16}$  years.<sup>2,3</sup> It has now been determined that the reduction potentials of these compounds<sup>13,14</sup> extend over 1.64 V, corresponding to  $158\ \text{kJ mol}^{-1}$  (Table 1).

A fairly linear correlation

$$E = (14.091 \pm 0.282) E^\circ_{\text{red}}(\text{AN}) - (0.279 \pm 0.188) \quad (r^2 = 0.993, n = 19) \quad (3)$$

is obtained (Figure 2) between the electrophilicity parameters  $E$  and  $E^\circ_{\text{red}}$ , the reduction potentials determined in acetonitrile (AN).

In view of the almost negligible effect of solvents on the rates of the reactions of benzhydrylium ions with uncharged nucleophiles,<sup>1a,15</sup> the finding that variation of the substituents affects the reduction potentials of benzhydryl cations in dichloromethane (DCM) to a greater extent (factor 1.35) than the reduction potentials in acetonitrile (AN) is remarkable (eq 4)

$$E^\circ_{\text{red}}(\text{DCM}) = (1.352 \pm 0.085) E^\circ_{\text{red}}(\text{AN}) + (0.159 \pm 0.040) \quad (r^2 = 0.966, n = 10) \quad (4)$$





















Since reduction potentials in dichloromethane (DCM) have only been determined for a limited amount of compounds, the further discussion will concentrate on the data determined in acetonitrile (AN).

Combination of eq 1 with the Eyring equation yields eq 5, which expresses the effect of electrophile variation ( $\partial E$ ) on the free energy of activation  $\Delta G^\ddagger$  for the reactions with a certain nucleophile whose slope parameter is  $s$ .

$$\partial \Delta G^\ddagger = -2.303RT \partial \log k = -2.303RT s \partial E \quad (5)$$

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**Table 1.** Electrophilicity Parameters ( $E$ ), One-Electron Reduction Potentials ( $E_{\text{red}}^{\circ}$ ) in Acetonitrile (AN) and Dichloromethane (DCM), LUMO Energies ( $\epsilon_{\text{LUMO}}$ ), Global Electrophilicity Values ( $\omega$ ), and Methyl Anion Affinities ( $\Delta E_0$ ) of Benzhydryl Cations and Related Quinone Methides

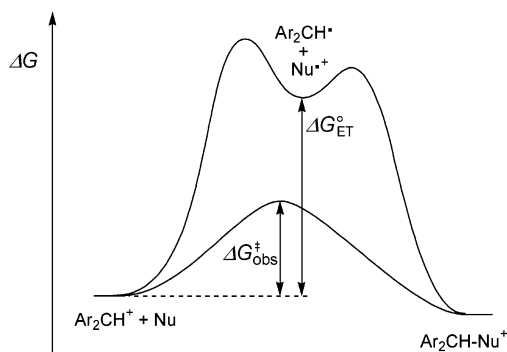
Electrophile	$E^a$	$E_{\text{red}}^{\circ}(\text{AN}),^b$ V	$E_{\text{red}}^{\circ}(\text{DCM}),^b$ V	$\epsilon_{\text{LUMO}},^c$ a.u.	$\omega,^c$ eV	$\Delta E_0,^d$ kJ mol $^{-1}$	
	Ph <sub>2</sub> CH <sup>+</sup>	5.90	0.35 <sup>e</sup>		-0.28171	13.00	-972.8
	tol(Ph)CH <sup>+</sup>	4.59	0.34 <sup>e</sup>		-0.27350	12.62	-954.8
	(tol) <sub>2</sub> CH <sup>+</sup>	3.63	0.24 <sup>e</sup>		-0.26604	12.29	-938.5
	ani(Ph)CH <sup>+</sup>	2.11	0.15 <sup>f</sup>		-0.26149	12.06	-928.5
	(pfa) <sub>2</sub> CH <sup>+</sup>	-3.14	-0.21				
	(mfa) <sub>2</sub> CH <sup>+</sup>	-3.85	-0.22				
	(dpa) <sub>2</sub> CH <sup>+</sup>	-4.72	-0.23				
	(mor) <sub>2</sub> CH <sup>+</sup>	-5.53	-0.32				
	(mpa) <sub>2</sub> CH <sup>+</sup>	-5.89	-0.38				
	(dma) <sub>2</sub> CH <sup>+</sup>	-7.02	-0.45				
	(pyr) <sub>2</sub> CH <sup>+</sup>	-7.69	-0.56				
	(thq) <sub>2</sub> CH <sup>+</sup>	-8.22	-0.57				
	(ind) <sub>2</sub> CH <sup>+</sup>	-8.76	-0.57				
	(jul) <sub>2</sub> CH <sup>+</sup>	-9.45	-0.64				
	(lil) <sub>2</sub> CH <sup>+</sup>	-10.04	-0.64				
	nitro( <i>t</i> Bu) <sub>2</sub> QM		-0.81				
	tol( <i>t</i> Bu) <sub>2</sub> QM	-15.83	-1.12				
	ani( <i>t</i> Bu) <sub>2</sub> QM	-16.11	-1.13				
	dma( <i>t</i> Bu) <sub>2</sub> QM	-17.29	-1.26				
	jul( <i>t</i> Bu) <sub>2</sub> QM	-17.90	-1.29				

<sup>a</sup> Electrophilicity parameters  $E$  of benzhydryl cations and quinone methides were taken from refs 2 and 3, respectively. <sup>b</sup> Reduction potentials  $E_{\text{red}}^{\circ}$  at 298 K vs SCE. <sup>c</sup> From ref 9, calculated at the B3LYP/6-31G(d) level of theory. <sup>d</sup> From ref 8, calculated at the B3LYP/6-31G(d,p) level of theory according to eq 2 with  $X^- = \text{CH}_3^-$ . <sup>e</sup> From ref 13. <sup>f</sup> From ref 14.

Multiplication with the Faraday constant  $F$  ( $= 96485$  C mol $^{-1}$ ) converts the reduction potential  $E_{\text{red}}^{\circ}$  into a free energy term as shown in eq 6.

$$\partial \Delta G_{\text{ET}}^{\circ} = -F \partial E_{\text{red}}^{\circ} \quad (6)$$

Division of eq 5 by eq 6 and substitution of  $\partial E$  by  $14.091 \partial E_{\text{red}}^{\circ}$  (from eq 3) yields eq 7, which indicates that 82%



**Figure 3.** Energy profiles for the polar and electron-transfer mechanism of electrophile–nucleophile combinations.

of the changes in the reduction potentials  $\Delta G^{\circ}_{\text{ET}}$  are realized as changes in the free energies of activation  $\Delta G^{\ddagger}$  of the reactions of a series of electrophiles with a nucleophile of  $s = 1.0$ .

$$(\partial \Delta G^{\ddagger} / \partial \Delta G^{\circ}_{\text{ET}}) = (2.303RT \, s \, \partial E) / (F \, \partial E^{\circ}_{\text{red}}) = 0.82s \quad (\text{at } 293 \text{ K}) \quad (7)$$

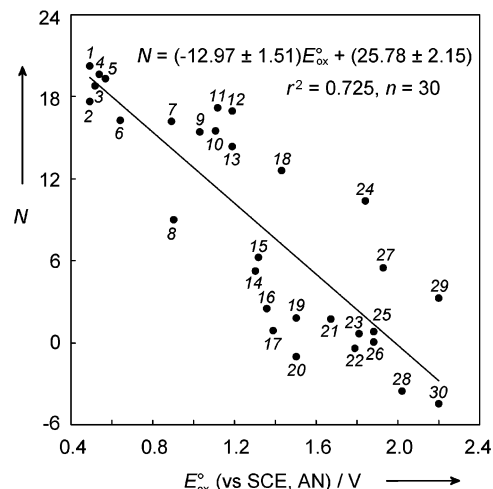
Though it is tempting to interpret this factor as an indication of 82% electron transfer in the transition state, the exact meaning of this value is more complicated, particularly since the changes in  $E^{\circ}_{\text{red}}$  appear to be solvent dependent (cf. eq 4). It is safe to conclude, however, that the degree of electron transfer in the transition states of the reactions of benzhydrylium ions with nucleophiles increases with the magnitude of the slope  $s$  as defined in eq 1.

It has previously been discussed<sup>13</sup> that the reactions of carbocations with  $\pi$ -systems cannot proceed via outer-sphere

**Table 2.** Oxidation Potentials  $E^{\circ}_{\text{ox}}$  and Reactivity Parameters  $N$  and  $s$  of Nucleophiles and the Calculated Free Energy Differences  $\delta \Delta G$  of the Electron Transfer and the Polar Mechanism at  $\log k_{\text{obs}} = -5$  and 8

entry	nucleophile	$E^{\circ}_{\text{ox}}$ (V vs SCE) <sup>a</sup>	$N$ <sup>b</sup>	$s$ <sup>b</sup>	$\delta \Delta G$ (kJ mol <sup>-1</sup> ) <sup>c</sup> at	
					$\log k_{\text{obs}} = -5$	$\log k_{\text{obs}} = 8$
1	(EtO <sub>2</sub> C) <sub>2</sub> CH <sup>-</sup> (DMSO)	0.49 <sup>d</sup> (ref 16)	20.22	0.65	136.7	72.7
2	(CH <sub>3</sub> CO) <sub>2</sub> CH <sup>-</sup> (DMSO)	0.49 <sup>d</sup> (ref 16)	17.64	0.73	113.3	64.2
3	CH <sub>3</sub> CO(CO <sub>2</sub> Et)CH <sup>-</sup> (DMSO)	0.52 <sup>d</sup> (ref 16)	18.82	0.69	127.0	70.8
4	CN(CO <sub>2</sub> Et)CH <sup>-</sup> (DMSO)	0.54 <sup>d</sup> (ref 17)	19.62	0.67	135.9	75.9
5	(CN) <sub>2</sub> CH <sup>-</sup> (DMSO)	0.57 <sup>d</sup> (ref 16)	19.36	0.67	136.9	77.1
6	dimedone anion (DMSO)	0.64 <sup>d</sup> (ref 16)	16.27	0.77	115.9	73.2
7	P( <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	0.89 (ref 18)	16.17	0.62	150.1	79.4
8	Me <sub>2</sub> C=C(OMe)OSiMe <sub>3</sub>	0.90 (ref 19)	9.00	0.98	81.8	63.6
9	P( <i>p</i> -MeC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	1.03 (ref 18)	15.43	0.64	156.8	90.6
10	PBu <sub>3</sub>	1.11 (ref 18)	15.49	0.69	161.1	105.0
11	piperidine (DMSO)	1.12 (ref 20)	17.19	0.71	172.3	119.8
12	morpholine (DMSO)	1.19 (ref 21)	16.96	0.67	180.4	120.4
13	PPh <sub>3</sub>	1.19 (ref 18)	14.32	0.65	163.9	99.8
14	1-(trimethylsilyloxy)cyclohexene	1.30 (ref 19)	5.21	1.00	93.7	77.4
15	H <sub>2</sub> C=C(OSiMe <sub>3</sub> )Ph	1.32 (ref 19)	6.22	0.96	104.0	83.9
16	1,3-dimethoxybenzene	1.36 (ref 13)	2.48	1.09	77.9	69.0
17	Me <sub>2</sub> C=CHCH <sub>2</sub> SiMe <sub>3</sub>	1.39 (ref 19)	0.90	1.17	67.8	64.6
18	P( <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>	1.43 (ref 18)	12.58	0.65	175.1	111.0
19	H <sub>2</sub> C=CHCH <sub>2</sub> SiMe <sub>3</sub>	1.50 (ref 19)	1.79	0.94	91.7	69.8
20	Me <sub>2</sub> C=CMe <sub>2</sub>	1.50 (ref 13)	-1.00	1.40	60.6	69.9
21	<i>p</i> -methylstyrene	1.67 (ref 22)	1.70	1.06	103.4	92.2
22	( <i>E</i> )-propenylbenzene	1.79 (ref 23)	-0.41	1.12	98.6	92.4
23	Me <sub>2</sub> C=CHMe	1.81 (ref 13)	0.65	1.17	106.7	103.4
24	P(OBu) <sub>3</sub>	1.84 (ref 18)	10.36	0.70	195.7	141.4
25	styrene	1.88 (ref 13)	0.78	0.95	121.1	100.1
26	1-methylcyclohexene	1.88 (ref 13)	0.08	1.15	110.0	105.5
27	P(OPh) <sub>3</sub>	1.93 (ref 18)	5.49	0.77	166.6	123.8
28	<i>m</i> -xylene	2.02 (ref 13)	-3.54	1.62	90.0	108.1
29	HSiMe <sub>2</sub> Ph	2.20 (ref 24)	3.27	0.73	179.9	130.8
30	toluene	2.20 (ref 13)	-4.47	1.32	105.9	111.3

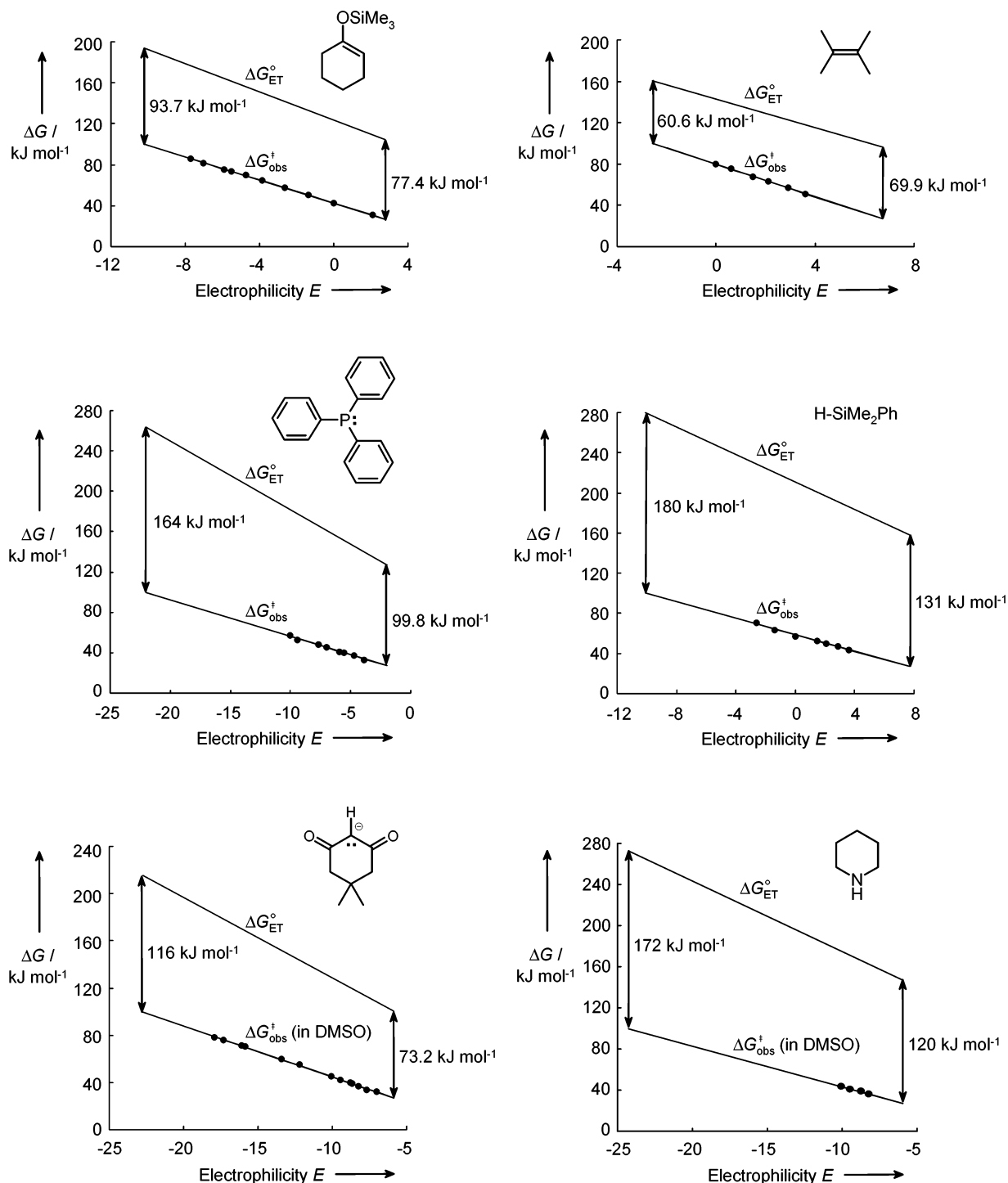
<sup>a</sup> In acetonitrile. <sup>b</sup>  $N$  and  $s$  parameters were taken from ref 2 for neutral  $\pi$ -nucleophiles and hydride donors, from ref 3 for carbanions, from ref 6 for amines, and from ref 25 for phosphorus nucleophiles. <sup>c</sup> At a given  $\log k_{\text{obs}}$ ,  $\delta \Delta G$  is calculated as the difference ( $\Delta G^{\circ}_{\text{ET}} - \Delta G^{\ddagger}_{\text{obs}}$ ). <sup>d</sup>  $E^{\circ}_{\text{ox}}$  was determined in DMSO and used without correction for the solvent.



**Figure 4.** Weak correlation of the nucleophilicities  $N$  of 30 reagents with their oxidation potentials  $E^{\circ}_{\text{ox}}$  (entry numbers + data from Table 2).

electron transfer because the observed free energies of activation for these reactions are much smaller than those expected for electron transfer (Figure 3). With the reduction potentials determined in this work, this analysis can now be generalized.

In previous work we already reported on the relationship between the electrophilicity parameters  $E$  and the reduction potentials  $E^{\circ}_{\text{red}}$  of a series of structurally variable carbocations.<sup>1c</sup> Because of the small correlation coefficient, we concluded that the driving force of the electron transfer cannot be the sole factor determining the rates of the combinations of carbocations with nucleophiles.<sup>1c</sup> This conclusion is corroborated by Figure 4, which shows that there is only a weak correlation between the



**Figure 5.** Comparison of the calculated free energies  $\Delta G_{ET}^{\circ}$  (eq 8) and  $\Delta G_{obs}^{\ddagger}$  for the reactions of nucleophiles with benzhydrylium ions in the range of  $\Delta G_{obs}^{\ddagger}$  from 100 to 27  $\text{kJ mol}^{-1}$  corresponding to  $-5 < \log k_2 < 8$ .

nucleophilicity parameters  $N$  and the oxidation potentials  $E^{\circ}_{ox}$  of different types of nucleophiles<sup>13,16–25</sup> (Table 2). Even after

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elimination of the anionic nucleophiles, where the work term in the Marcus equation cannot be neglected, a poor correlation remains, showing that electron transfer is not the only term controlling the nature of the transition states. The good correlation between the electrophilicity parameters  $E$  of benz-

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hydrolyium ions and quinone methides with their reduction potentials shown in Figure 2 allows us, however, to analyze these reaction series in greater detail.

In eq 8,  $E_{\text{red}}^{\circ}$  of the benzhydrylium ions is substituted by the corresponding electrophilicity parameters  $E$  (from eq 3) to yield the free enthalpies of electron transfer,  $\Delta G_{\text{ET}}^{\circ}$ , as a function of the electrophilicity parameters  $E$ .

$$\Delta G_{\text{ET}}^{\circ} = F(E_{\text{ox}}^{\circ} - E_{\text{red}}^{\circ}) = 96.5E_{\text{ox}}^{\circ} - 1.91 - 6.85E \quad (8)$$

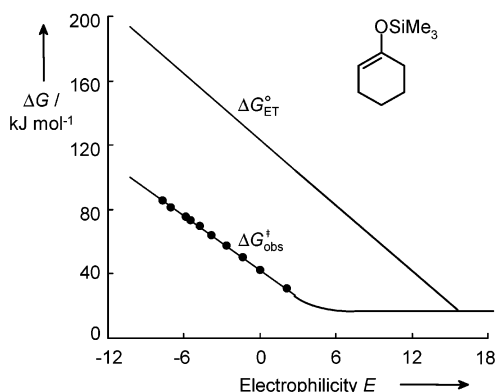
This relationship is graphically shown for six representative nucleophiles (reductants) by the upper correlation lines in the diagrams of Figure 5. All diagrams show that the actually observed free energies of activation for the corresponding electrophile–nucleophile combinations ( $\Delta G_{\text{obs}}^{\ddagger}$ ) are considerably smaller than  $\Delta G_{\text{ET}}^{\circ}$ . It should be noted that the experimentally observed range (marked by the actually measured data points) is extrapolated in all diagrams of Figure 5 to range from  $\Delta G^{\ddagger} = 100$  to  $27 \text{ kJ mol}^{-1}$ , corresponding to second-order rate constants of  $k = 1 \times 10^{-5}$  (left) and  $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (right), respectively, at  $20 \text{ }^{\circ}\text{C}$ . These borders have been selected in order to cover the whole relevant range of reactivities from the slowest bimolecular reactions observable in practice to the fastest reactions which follow eq 1, only 1–2 orders of magnitude below the diffusion limit. Depending on the strengths of the nucleophiles, variable groups of electrophiles have to be selected for matching this range.

One can see that the two correlation lines never cross (see also Table 2), indicating that in the considered range the electrophile–nucleophile combinations always proceed considerably faster than electron transfer, i.e., outer-sphere electron transfer does not play a role in any of these reactions, since the activation free energies of outer-sphere electron transfer must be larger than the free energy change of electron transfer. In the case of adiabatic outer-sphere electron transfer, the interaction energy at the intersection of potential surfaces is ca.  $1 \text{ kJ mol}^{-1}$ . In contrast, the energy difference between  $\Delta G_{\text{obs}}^{\ddagger}$  and  $\Delta G_{\text{ET}}^{\circ}$  ( $60.9$ – $180 \text{ kJ mol}^{-1}$ ) in Figure 5 is by far larger than the interaction energy of adiabatic outer-sphere electron transfer.

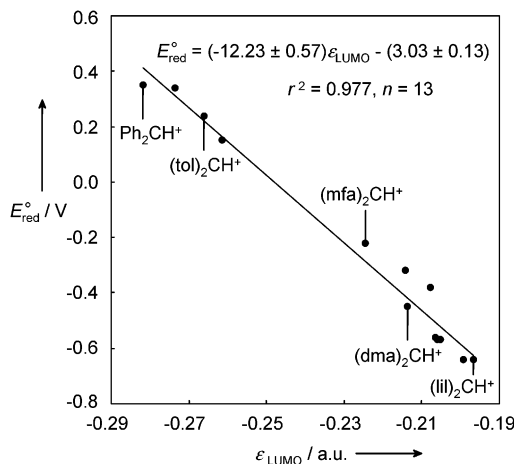
Equation 7 implies that the two correlation lines will be parallel for  $0.82s = 1$ , i.e., for  $s = 1.22$ . For most nucleophiles the slope parameter  $s$  is smaller than 1.22; consequently, for most electrophile–nucleophile combinations the differences between the free energy of electron transfer and the activation free energy of the polar reaction decrease with increasing electrophilicity, but even at a rate constant of  $k = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , there is a considerable gap between the two lines for all nucleophiles listed in Table 2. Since a further increase of electrophilicity does not increase the rate of the polar reaction above  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (diffusion limit) but the driving force of electron transfer, one can extrapolate the point where outer-sphere electron transfer may become important (Figure 6).

One-electron reduction implies transfer of an electron into the LUMO of the electrophile. For that reason, the reduction potentials  $E_{\text{red}}^{\circ}$  correlate with the energies of the LUMOs,  $\epsilon_{\text{LUMO}}$ , for a series of benzhydrylium ions<sup>9</sup> (Figure 7).

Multiplication of  $E_{\text{red}}^{\circ}$  with the Faraday constant  $F$  converts the reduction potential into a free energy term (eq 6) and shows that 45% of the differences in  $\epsilon_{\text{LUMO}}$  are observable as differences in the reduction potentials. Though the magnitude of this fraction cannot easily be interpreted because it includes



**Figure 6.** Comparison of  $\Delta G_{\text{obs}}^{\ddagger}$  and the calculated free energies  $\Delta G_{\text{ET}}^{\circ}$  (eq 8) for reactions of benzhydrylium ions with 1-(trimethylsilyloxy)cyclohexene ( $s = 1.00$ ).



**Figure 7.** Correlation of the one-electron reduction potentials  $E_{\text{red}}^{\circ}$  (vs SCE, AN, 298 K) of benzhydrylium ions with their LUMO energies  $\epsilon_{\text{LUMO}}$  (calculated at the B3LYP/6-31G(d) level of theory, from ref 9).

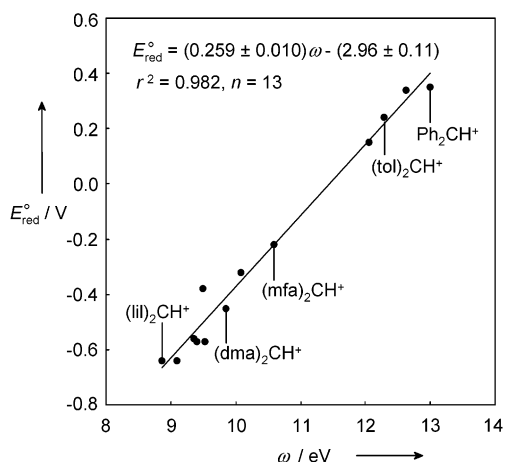
solvation effects, the high value of the correlation coefficient shows a tight relation between the two quantities.

An even better correlation is observed between the reduction potentials and Parr's global electrophilicity parameters  $\omega$ ,<sup>26</sup> which have been calculated for these benzhydrylium ions by Pérez and co-workers.<sup>9</sup> Though the global electrophilicity has been defined<sup>26</sup> as  $\omega = \mu^2/2\eta$  ( $\mu$  = electronic chemical potential,  $\eta$  = chemical hardness) and therefore has the dimension of an energy, the physical meaning of the slope of the correlation in Figure 8 is not yet clear.

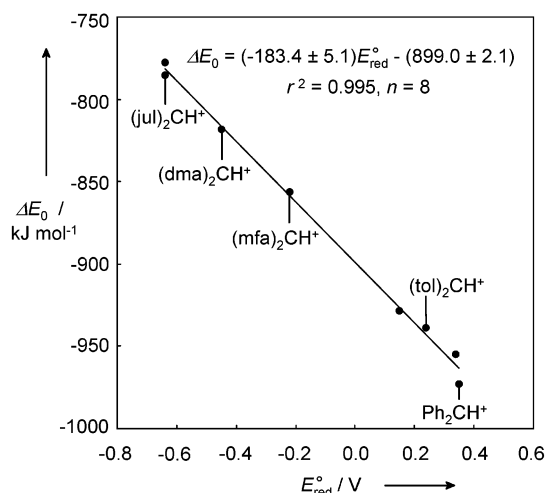
As pointed out above, the correlation between the electrophilicity parameter  $E$  and the reduction potentials  $E_{\text{red}}^{\circ}$  is due to the fact that the combination of benzhydrylium ions with  $X^-$  involves the shift of an electron from the nucleophile to the electrophile. For the same reason, the calculated methyl anion affinities<sup>8</sup> ( $\Delta E_0$  for eq 2,  $X^- = \text{CH}_3^-$ ) correlate perfectly with the reduction potentials (Figure 9).

When the reduction potentials are replaced by the corresponding free energies, one can derive that the changes in calculated methyl anion affinities (gas phase) are 1.9 times those of the changes of free energies for one-electron transfer in acetonitrile. As pointed out previously,<sup>8</sup> the large differences in Lewis acidities in the gas phase are reduced to 62 % in

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**Figure 8.** Correlation between the one-electron reduction potentials  $E_{\text{red}}^{\circ}$  (vs SCE, AN, 298 K) of benzhydrylium ions and their global electrophilicity parameters  $\omega$  (from ref 9).



**Figure 9.** Correlation of the methyl anion affinities  $\Delta E_0$  (eq 2,  $X = \text{CH}_3^-$ , from ref 8) with the one-electron reduction potentials  $E_{\text{red}}^{\circ}$  (vs SCE, AN, 298 K) of benzhydrylium ions.

dichloromethane solution, which implies that substituent variation in benzhydrylium ions affects their Lewis acidities (anion affinities) only slightly more (factor 1.2) than their reduction potentials.

How do these interpretations match with Arnett's reports that reactions of carbocations with carbanions may proceed via electron transfer, because in some cases dimers derived from the carbanions have been isolated? Our analysis is restricted to ester-, keto-, and cyano-stabilized carbanions (entries 1–6 in Table 2). In agreement with our product studies and our conclusion that outer-sphere electron transfer does not occur with such anions, Arnett also did not find products of oxidative dimerization of carbanions when combining carbanions of that type with crystal violet, malachite green, or tropylium ions.<sup>27</sup> Mixtures of such carbanions with the carbocations either persisted (unfavorable equilibrium) or led to covalent carbocation–carbanion adducts.<sup>27</sup>

Oxidative dimerization was observed, however, when the *p*-tolylmalodinitrile anion was combined with the tropylium ion

or the tris(*p*-methoxy)tritylium ion.<sup>27</sup> Preliminary kinetic experiments (in the München laboratory) suggest nucleophilicity parameters of  $N \approx 15$  and  $s \approx 1.1$  for this carbanion in DMSO. Its lower  $N$  parameter is in accord with the higher acidity of *p*-tolylmalodinitrile ( $\text{p}K_{\text{a}} = 4.85$ )<sup>17</sup> compared with malodinitrile ( $\text{p}K_{\text{a}} = 11.0$ ,<sup>17</sup>  $N = 19.4$ )<sup>3</sup> and ethyl cyanoacetate ( $\text{p}K_{\text{a}} = 13.1$ ,<sup>17</sup>  $N = 19.6$ )<sup>3</sup>. Despite its lower  $N$  value, one still expects diffusion control for the polar reactions of the *p*-tolylmalodinitrile anion with the tropylium ion ( $E = -3.72$ )<sup>4</sup> or the tris(*p*-methoxy)-tritylium ion ( $E = -4.35$ )<sup>6</sup> in DMSO.

While being a weaker nucleophile, the *p*-tolylmalodinitrile anion is a considerably stronger reductant than the malodinitrile anion ( $\Delta\Delta E_{\text{red}}^{\circ} = 0.217$  V)<sup>17</sup> or the ethyl cyanoacetate anion ( $\Delta\Delta E_{\text{red}}^{\circ} = 0.188$  V).<sup>17</sup> Though we follow Arnett's recommendation not to calculate standard free energies for the electron transfer from arylmalodinitrile anions to carbocations because of the problems to determine reversible oxidation potentials for these anions, it is obvious that the probability of observing electron transfer is much higher in the case of aryl-substituted carbanions, and it is this type of carbanion where the change from the polar to the electron-transfer mechanism can be expected.

It should be noted, however, that the observation of oxidative dimerization of carbanions does not necessarily prove that the corresponding carbocation–carbanion combinations proceed via electron transfer. Since combinations of stabilized carbocations with stabilized carbanions are reversible, the carbanion dimers may also arise from decomposition of initially formed covalent adducts. In the case of highly stabilized trityl cations and anions, it was even possible to observe the coexistence of ions and radicals.<sup>28</sup>

## Conclusions

Though the electrophilic reactivities of benzhydrylium ions, as expressed by their empirical electrophilicity parameters  $E$ , correlate perfectly with their reduction potentials, one can definitely exclude outer-sphere electron transfer to occur in activation-controlled reactions of benzhydrylium ions with the nucleophiles listed in Table 2. Inner-sphere electron transfer which involves a significant interaction energy at the intersection point may be an alternative description of the electrophile–nucleophile combinations. However, the clear distinction between the polar reaction and inner-sphere electron transfer is difficult at present.

**Acknowledgment.** This paper is dedicated to Professor R. W. Hoffmann on the occasion of his 70th birthday. Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Grant-in-Aid for Scientific Research Priority Area (No. 13031059) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, is gratefully acknowledged.

**Supporting Information Available:** Second-harmonic AC voltammograms of diarylcarbenium ions in acetonitrile and dichloromethane and of quinone methides in acetonitrile (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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