Reaction of Dioxetane 1c with Potassium Superoxide. A sample of 105 mg (0.458 mmol) of dioxetane **1c** in 3 mL of dry acetonitrile was added to a suspension of 50.0 mg (0.703 mmol) of potassium superoxide in 5 mL of dry acetonitrile, which contained ca. 10 mol % of 18-crown-6. After 15 min, the dioxetane had disappeared (negative KI test), and 5 mL of water was added. Extraction with CH_2Cl_2 was followed by drying over $MgSO_4$ and evaporation of the solvent at 20 °C/15 Torr to yield 64.3 mg (93%) of epoxy alcohol **8c** as the only product (by ^1H NMR).

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 172 "Molekulare Mechanismen kanzerogener Primärveränderungen"), the Wilhelm-Sander Stiftung, and the Fonds der Chemischen Industrie.

Registry No. 1a, 35322-45-3; **1b**, 136749-73-0; **1c**, 136132-07-5; **1d**, 40814-69-5; **2b**, 141248-81-9; **2c**, 141248-82-0; **2d**, 141248-83-1; **3b**, 141248-84-2; **3d**, 141248-85-3; **4c**, 141248-86-4; **5c**, 141248-87-5; **6c**, 141248-88-6; **7c**, 64398-73-8; **8c**, 141248-89-7; **9c**, 141248-90-0; **9d**, 141248-91-1; **9d'**, 141248-92-2; **10c**, 141248-93-3; **11c**, 141248-94-4; **11d**, 92527-70-3; **12a**, 98-86-2; **12b**, 532-27-4; **12c**, 70-11-1; **12d**, 102-04-5; DABCO, 280-57-9; $(i\text{-}Pr)_2NH$, 75-31-0; CN^-, 57-12-5; Br^-, 24959-67-9; Cl^-, 16887-00-6; NEt_3, 121-44-8; PhSH, 108-98-5; $PhCH_2SH$, 100-53-8; Ph_2S, 139-66-2; SCN^-, 302-04-5; OH^-, 14280-30-9; $O_2^{\bullet-}$, 11062-77-4; morpholine, 110-91-8.

Homolytic and Heterolytic Cleavage Energies for Carbon-Nitrogen Bonds

Edward M. Arnett,* Sampath Venimadhavan, and Kalyani Amarnath

Contribution from the Department of Chemistry, Duke University, Durham, North Carolina 27706. *Received November 13, 1991*

Abstract: Using calorimetric and electrochemical techniques described in previous reports, we have determined the heterolytic and homolytic bond energies at 25 °C in sulfolane for the carbon-nitrogen bonds in the compounds produced by reactions of nine resonance-stabilized carbenium ions with nitranions formed by deprotonating the following nitrogen acids: succinimide, phthalimide, carbazole, and 3,6-dibromocarbazole.

Introduction

In a series of recent publications,[1-6] we have reported heterolytic bond energies (ΔH_{het}'s) derived from the calorimetric heats of reaction of resonance-stabilized carbenium ions with various types of anions and neutral compounds at 25 °C in tetramethylene sulfone (sulfolane), a highly polar solvent with unusual resistance to attack by both acids and bases. Heats of heterolysis (ΔH_{het}'s) were obtained directly from the heats of reaction of the carbenium ions and anions simply by changing the sign, and over 200 values have been obtained for carbon-carbon, carbon-oxygen, and carbon-sulfur bonds. Most of the ΔH_{het}'s obtained in this way were converted into homolytic bond energies (ΔH_{homo}'s) through the use of the thermodynamic cycle shown in Scheme I.

The free energy of electron transfer (ΔG_{ET}), which relates ΔH_{homo} to ΔH_{het}, is derived from the oxidation potential of the anion and the reduction potential of the carbenium ion. In turn, these important values have been obtained in our laboratory by several voltammetric techniques: ordinary cyclic voltammetry, second-harmonic ac voltammetry, and Osteryoung square-wave voltammetry (OSWV).[5] In view of the instability of the radicals derived by oxidation and reduction of the anions and carbenium ions, much effort was employed in obtaining reversible redox potentials by the methods listed above. In general, there was remarkably good agreement between results obtained by the three methods, even though in some cases the redox potentials were irreversible by one or another of the techniques. However, in the present study involving carbenium ions and nitranions, we have used only CV and SHACV for all our electrochemical measurements.

Scheme I. Thermodynamic Cycle Relating Homolytic and Heterolytic Bond Energies to Electron-Transfer Energies

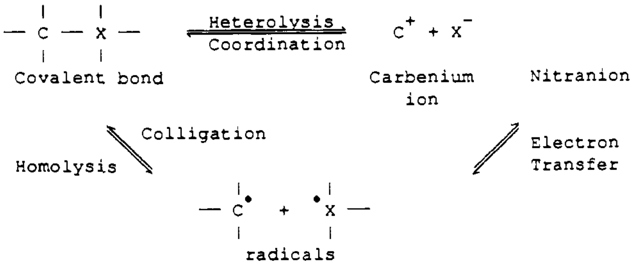
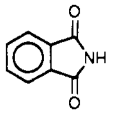
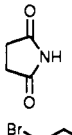
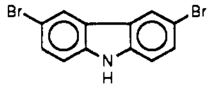
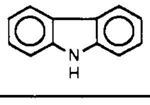


Table I. Structures of Nitranion Precursors

compound	structure
phthalimide	
succinimide	
3,6-dibromocarbazole	
carbazole	

The second important concern in combining calorimetric enthalpies with electrode potentials is that the latter properties are free energy terms. In some of our earlier work,[2,5] we demonstrated that entropies of electron transfer for a number of compounds were remarkably small so that enthalpies and free energies of electron transfer could be used almost interchangeably. The entropies of

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0002-7863/92/1514-5598$03.00/0

Table II. Oxidation Potentials of the Nitranions in Sulfolane/3-Methylsulfolane (5%) in the Temperature Range 25–35 °C

	oxidation potentials (V)[a] at		
anion of	25 °C	30 °C	35 °C
phthalimide	−0.155	−0.158	−0.159
succinimide	−0.108	−0.109	−0.112
3,6-dibromocarbazole	−0.129	−0.128	−0.131
carbazole	−0.346	−0.350	−0.352

[a] $E_{1/2}$ values obtained by CV. All values referenced to the ferrocene/ferrocenium redox couple using a Pt working electrode, a Ag/$AgNO_3$ reference electrode, and a Pt auxiliary electrode. Scan rate at 25 °C in 25 mV/s; at 30 and 35 °C, scan rates are 50 mV/s; standard deviation = ±25 mV.

electron transfer were determined from the temperature coefficients of the redox potentials and were found to be negligible. This was accomplished for the carbenium ions and the four nitranions used to produce the compounds reported here (Tables I and II).

We now wish to report results for a series of compounds with carbon–nitrogen bonds derived from the reactions of the resonance-stabilized carbenium ions with nitranions produced by deprotonation of four nitrogen acids (Table I) with potassium hydride in sulfolane solution at 25 °C. The pK_a's for acidic dissociation of these compounds have been determined in dimethyl sulfoxide, using the potassium salt of the solvent, by Bordwell's group.[7] Such values are directly convertible into free energies of heterolytic cleavage for the N–H bonds. Correspondingly, Bordwell's group has determined homolytic free energies of dissociation (BDE's) for some N–H bonds by combining the pK_a's with the oxidation potentials of the nitranions.[8] We find that the BDE values reported here agree quite well with those of Bordwell (Table IV).

The question then arises as to how these properties of the N–H bonds are related to those of equivalent N–C bonds in the neutral compounds, where the same anions have become bound to a series of resonance-stabilized carbenium ions.

Experimental Section

Purification of the Solvents. Sulfolane (Phillips Petroleum Co.) was stirred with NaOH pellets overnight at 100–150 °C while argon was bubbled through the solvent. The sulfolane was decanted and stirred with warming overnight with CaH_2 under an argon atmosphere. The dry solvent was then vacuum-distilled (bp = 110–111 °C at 1 Torr), and the first 10% of the distillate was discarded. Upon solidifying, the pure, dry sulfolane (mp = 28.5 °C)[9] formed a colorless, transparent glass, which was protected from contact with air. Its melting point was lowered for work at 25 °C by the addition of 3-methylsulfolane.

3-Methylsulfolane (Aldrich) was stirred overnight at room temperature with CaH_2 under an argon atmosphere and then vacuum-distilled (bp = 101–102 °C at 1 Torr). The purified solvent was transferred to an argon-filled drybox, where the melted sulfolane and 3-methylsulfolane were mixed to form a 5% 3-methylsulfolane/95% sulfolane solvent mixture (v/v). This mixture was stirred over CaH_2 for 1 day, filtered, and degassed by the freeze–thaw method. We have been informed by the technical experts at BAS, West Lafayette, IN, that unless the water content is below 30 ppm, it is impossible to get reliable voltammetric responses for these unstable species. This is well below the level which can be detected by Karl Fischer titrimetry.

Purification of Potassium Hydride. An oil dispersion of potassium hydride (Fluka) was washed thoroughly with dry pentane under an argon atmosphere to remove the mineral oil. The resulting hydride powder was dried under vacuum and then transferred to an argon-filled drybox.

Preparation of the Carbenium Ions. Triphenylcarbinol (Aldrich), triphenylcyclopropene (Alfa), 9-phenyl-9-xanthenol (Fluka), and xanthene (Aldrich) were converted to the corresponding tetrafluoroborate salts by the procedures described by Dauben et al.[10] The carbenium ions were washed with anhydrous ethyl ether and dry, ice-cold chloroform under an argon atmosphere. Commercially available tropylium tetrafluoroborate (Aldrich) was recrystallized twice from CH_3CN/Et_2O.

The dianisylmethylium ion (DPM^+) was prepared by a modified version of Dauben's procedure.[10] 4,4′-Dimethoxybenzhydrol (1.974 g, 8 mmol) was dissolved in a mixture of 25 mL of dry ether and 5.1 mL (~40 mmol) of propionic anhydride. An 85% ether solution of $HBF_4{\cdot}OEt_2$ (3.05 g, ~16 mmol) was added. The resulting solution was stirred at room temperature for 20 min and then in an ice bath for 10 min. The resulting reddish-purple precipitate was filtered off under argon and washed with cold, dry ether and cold, dry pentane. The compound was dried under vacuum (mp = 98 °C dec). It is stable inside the drybox up to 1 week.

The 9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium ion (DPA^+) was synthesized by a six-step procedure from α-phenyl-*o*-toluic acid in an overall yield of 33%. A literature method[11] was modified to prepare the 9,9-dimethyl-10-anthrone; a general Grignard procedure was followed to prepare the corresponding carbinol [mp = 164.5–165.5 °C (lit.[12] mp = 167.5–168.5 °C)]. A procedure similar to the one used for the preparation of the dianisylmethylium ion was followed in the last step. The carbenium ion was characterized by NMR spectroscopy in $CDCl_3$ (300 MHz): δ 1.98 (s, CH_3), 7.60–8.38 (m, arom H). The yellow carbenium ion (mp = 191 °C dec) was shown to be more than 99% pure by NMR spectroscopy. The pK_{R^+} value of this carbenium ion was determined to be −5.49 (±0.06) by monitoring the changes of its absorption with the changes of the acid concentrations of the solvents, according to the method of Arnett and Bushick.[13]

2,4,6-Triphenylpyrylium tetrafluoroborate ($(TPP)BF_4$) (Alfa) was recrystallized from 1,2-dichloroethane and dried in a vacuum oven at 80 °C for 4 h, forming yellow needles [mp = 251–257 °C (lit.[14] mp = 251–257 °C)].

Perinaphthene was prepared by the procedure of Bondjouk and Johnson.[15] The product, a pale yellow compound (99% 1*H*-phenalene with 3% saturated analogue and no other impurities), was dried in a vacuum oven and stored inside the drybox (mp = 84–85 °C). The compound was characterized by NMR spectroscopy. Perinaphthenium tetrafluoroborate ($(PNA)BF_4$) was obtained from 1*H*-phenalene by hydride transfer with trityl tetrafluoroborate in CH_2Cl_2 at −10 °C under argon. The solution was cooled to −78 °C for 20 min and filtered at −78 °C under argon. The dark yellow powder, which becomes dark green after some time, was warmed slowly to 0 °C and then transferred to the drybox. The carbenium ion was characterized by NMR spectroscopy.

Preparation and Purification of the Anion Precursors. Succinimide (Aldrich) was recrystallized twice from hot water, phthalimide (Aldrich) was purified by recrystallization from absolute ethanol, and carbazole and 3,6-dibromocarbazole (Aldrich) were recrystallized three times from dry benzene.

Generation of the Nitranions. The anion precursor (0.04–0.06 g) was dissolved in 35 mL of degassed 5% 3-methylsulfolane/95% sulfolane, and then an excess amount (0.02–0.04 g) of KH was added. All of the operations for preparing the anion solutions were carried out inside an argon-filled, oxygen-free drybox. The mixture was stirred for about 30–60 min at room temperature. The anion solution was then filtered directly into the reaction vessel of the calorimeter.

Calorimetry. Heats of reaction of the various carbenium ions with the nitranions in the sulfolane solvent mixture were measured with a Tronac 450 titration calorimeter at 25 °C. The operation of the calorimeter was checked periodically by measuring the heat of neutralization of an aqueous solution of sodium hydroxide with a standard aqueous HCl solution.

The solutions of the carbenium ions (0.08–0.1 M) were prepared inside the argon-filled drybox with an analytical balance and volumetric flask. Before each calorimetric run, the calibrated motor-driven buret, filled with the carbenium ion solution, and the reaction vessel, containing about 35 mL of the nitranion solution (~0.04 M), were connected to the calorimeter insert assembly. A dry argon blanket was maintained at the top of the reaction vessel to protect the nitranion solution/solvent from exposure to air. The operation of the calorimeter itself has been described in detail elsewhere.[16] All the heat measurements were conducted in the

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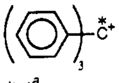
Table III. Redox Potentials (V) of Nitranions in Sulfolane/3-Methylsulfolane (5%) at 25 °C

anion of	E_{ox}[a]	$E_{1/2}$[b]	technique and conditions[c]
phthalimide	−0.155 ± 0.005	−0.176 ± 0.009	SHACV, Pt electrode, 6°/96°, ac amplitude 140 mV, frequency 25 Hz
succinimide	−0.108 ± 0.012	−0.124 ± 0.015	SHACV, Pt electrode, 10°/100°, ac amplitude 140 mV, frequency 40 Hz
3,6-dibromocarbazole	−0.129 ± 0.009	−0.160 ± 0.010	SHACV, Pt electrode, 8°/98°, ac amplitude 100 mV, frequency 25 Hz
carbazole	−0.346 ± 0.010	−0.352 ± 0.014	SHACV, Pt electrode, 16°/106°, ac amplitude 140 mV, frequency 40 Hz

[a] All E_{ox} values obtained by CV at a scan rate of 25 mV/s under an argon blanket. [b] SHACV scan rate is 5 or 10 mV/s. [c] All values reported vs ferrocenium/ferrocene $E_{1/2}$ values as obtained under identical conditions. All solutions are 1.5–5.0 mM in anion concentration. All values obtained at 25 °C using a Ag/AgNO$_3$ reference electrode and a Pt auxiliary electrode. Counterion is K$^+$.

Table IV. Heats of Heterolysis, Heats of Homolysis, Free Energies of Electron Transfer, and Bond Dissociation Energies (kcal/mol) and AOP's for Reactions of the Trityl Cation with Nitranions in Sulfolane/3-Methylsulfolane (5%) at 25 °C

cation =

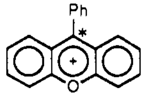


trityl[a]

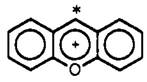
nitranion of	pK_a[b]	$E_{1/2}$ (V)[c]	AOP[d]	ΔH_{het}[e]	ΔG_{ET}	ΔH_{homo}[f]	BDE[g]
phthalimide	13.66	−0.176 ± 0.009	14.66	31.69 ± 0.45	−0.99 ± 0.26	30.70 ± 0.52	89.1
succinimide	14.67	−0.124 ± 0.015	17.24	32.39 ± 0.70			91.7
3,6-dibromocarbazole	17.16	−0.160 ± 0.010	19.82	39.84 ± 0.89	−0.62 ± 0.28	39.22 ± 0.93	94.3 (93.5)[h]
carbazole	19.92	−0.352 ± 0.014	19.17	42.91 ± 0.71	−5.05 ± 0.36	37.86 ± 0.80	93.6 (92.7)[h]

[a] pK_{R^+} = −6.63, CRP = 12.2, $E_{1/2}(C^+)$ = −0.133 ± 0.007 V. [b] Values from ref 7. [c] Measured in a BAS 100A electrochemical analyzer in sulfolane/3-methylsulfolane at 25 °C by cyclic voltammetry or second-harmonic ac voltammetry. [d] AOP = 1.37pK_a + 23.06$E_{1/2}$. [e] ΔH_{het} measured using titration calorimetry at 25 °C. $\Delta H_{het} = -\Delta H_{reacn}$ (kcal/mol). [f] Calculated using the equation $\Delta H_{homo} = \Delta H_{het} + \Delta G_{ET}$ where $\Delta G_{ET} = 23.06[E_{1/2}(N^-) - E_{1/2}(C^+)]$. [g] BDE = 1.37p$K_a$ + 23.06$E_{ox}(N^-)$ + 55.86; E_{ox} values referred to SHE by adding +0.8 V to the values referred to the Ag/AgNO$_3$ reference electrode. [h] Values from ref 8.

Table V. Heats of Heterolysis, Heats of Homolysis, and Free Energies of Electron Transfer (kcal/mol) for Reactions of 9-Phenylxanthylium and Xanthylium Ions with Nitranions in Sulfolane/3-Methylsulfolane (5%) at 25 °C



9-phenylxanthylium[a]



xanthylium[b]

	9-phenylxanthylium[a]			xanthylium[b]		
nitranion of	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
phthalimide	20.60 ± 0.37	4.06 ± 0.26	24.66 ± 0.45	29.02 ± 0.39	3.94 ± 0.31	32.96 ± 0.50
succinimide	22.67 ± 0.66	5.26 ± 0.38	27.93 ± 0.76	30.34 ± 0.89	5.14 ± 0.42	35.48 ± 0.98
3,6-dibromocarbazole	27.48 ± 1.30	4.43 ± 0.28	31.91 ± 1.33	35.79 ± 0.81	4.31 ± 0.33	40.10 ± 0.87
carbazole	34.58 ± 0.29			40.29 ± 0.48		

[a] pK_{R^+} = 1.1, CRP = 6.84, $E_{1/2}(C^+)$ = −0.352 ± 0.007 V. [b] pK_{R^+} = −0.85, CRP = 9.15, $E_{1/2}(C^+)$ = −0.347 ± 0.010 V.

isoperibolic mode at 25 °C. Each reported ΔH_{reacn} value is the average of five to seven enthalpy measurements with the same stock solution of the carbenium ion. Reproducibility of the ΔH_{reacn} results was verified by using different samples of the carbenium ion and nitranion solutions prepared on different days over a period of several months. A heat of heterolysis (ΔH_{het}) can be obtained from a ΔH_{reacn} simply by changing its sign.

Product Analysis. Products were analyzed by HPLC, NMR spectroscopy, and elemental analysis after isolation.[17]

Electrochemical Measurements. Tetrabutylammonium tetrafluoroborate ((TBA)BF$_4$) was recrystallized (1/5 ethanol/water) triply and vacuum-dried at 60 °C for 24 h before use. A 0.1 M solution of (TBA)BF$_4$ was used as the supporting electrolyte for all the electrochemical measurements. All the redox potentials were measured by using a BAS 100A electrochemical analyzer (BAS, West Lafayette, IN) equipped with a three-electrode assembly. The platinum working electrode (BAS) was polished with a BAS polishing diamond suspension and rinsed with ethanol and acetone before each run. The counter electrode was a platinum wire (BAS). The silver/silver nitrate reference electrode was made by inserting a silver wire (o.d. = 1 mm; Aldrich; 99.99+%) into a 0.1 M solution of AgNO$_3$, which was isolated from the electrolyte solution by a fritted-glass bridge (Vycor membrane). Solvent used in the electrochemical experiment was used to dissolve the AgNO$_3$. The ferrocenium/ferrocene redox couple was used as the internal standard for all the electrochemical measurements, and its redox potential was checked against the reference electrode before and after the experiments. A BAS-supplied electrical cell was used in the measurements.

The preparation of the carbenium ion solutions and the determination of their $E_{1/2}$(red) values have been described previously.[2]

Preparation of Nitranion Solutions. The sample of nitrogen acid (enough for making 10 mL of a 1.5 mM solution) was weighed into the electrical cell inside the drybox. The cell was transferred quickly to the BAS cell stand and flushed with ultrapure argon for 1–2 min. Ten milliliters of the 0.1 M supporting electrolyte solution was added to the cell via a Hamilton airtight syringe, and the solution was again flushed with ultrapure argon. An appropriate amount of potassium dimsyl solution sufficient to generate a 1.5 mM solution of the anion was added to the cell, and the electrochemical measurements were made immediately thereafter.

Voltammetric Methods. Two voltammetric techniques, namely cyclic voltammetry (CV) and second-harmonic ac voltammetry (SHACV), were used to determine the redox potentials. While CV gave irreversible potentials, reversible oxidation potentials were obtained for the nitranions using SHACV. The techniques and the experimental conditions are listed in Table III. The maximum errors in CV measurements for a scan rate of 25 mV/s and in SHACV measurements for scan rates of 5–10 mV/s were ±25 mV.

Much difficulty was encountered in obtaining the oxidation potentials of these highly unstable anions. In response to helpful criticisms of the SHACV techniques by an expert reviewer, we wish to add the following comments: (a) In all cases reported here, the I and Q traces were brought to a point of intersection at zero current on the potential axis. (b) High frequencies were avoided in favor of those which have been used successfully for phenoxide, thiophenoxide, and fluorenide ions, for which we have independent corroboration of our oxidation potentials by different voltammetric methods. (c) In some cases, higher amplitude measurements were tried but with little effect on the oxidation potential. (d) Several results were cross-checked by ordinary cyclic voltammetry and the Osteryoung square-wave technique (OSWV), with agreement within experimental error.

In our hands, SHACV has been a useful alternative or check on CV but, being a slow ac technique, is less reliable than OSWV. Moreover, in most instances, the potentials we have reported are those due to res-

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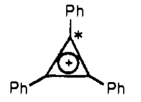
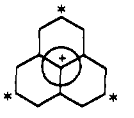
Table VI. Heats of Heterolysis, Heats of Homolysis, and Free Energies of Electron Transfer (kcal/mol) for Reactions of Triphenylcyclopropenylium and Tropylium Cations with Nitranions in Sulfolane/3-Methylsulfolane (5%) at 25 °C

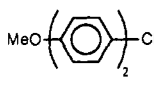


nitranion of	triphenylcyclopropenylium[a]			tropylium[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
phthalimide	23.88 ± 0.18	26.01 ± 0.21	49.89 ± 0.28	23.05 ± 0.35	10.28 ± 0.21	33.33 ± 0.41
succinimide	26.49 ± 0.36	27.21 ± 0.35	53.70 ± 0.50	25.12 ± 0.37	11.48 ± 0.35	36.60 ± 0.51
3,6-dibromocarbazole	27.27 ± 1.17	26.38 ± 0.24	53.65 ± 1.19	26.87 ± 0.19	10.65 ± 0.23	37.52 ± 0.30
carbazole	32.19 ± 0.44	21.95 ± 0.33	54.14 ± 0.55	30.77 ± 0.55	6.23 ± 0.32	37.00 ± 0.64

[a] $pK_{R^+} = 3.1$, CRP = 25.8, $E_{1/2}(C^+) = -1.304 \pm 0.003$ V. [b] $pK_{R^+} = 4.7$, CRP = 7.90, $E_{1/2}(C^+) = -0.620 \pm 0.002$ V.

Table VII. Heats of Heterolysis, Heats of Homolysis, and Free Energies of Electron Transfer (kcal/mol) for Reactions of Perinaphthenium and Bis(4-methoxyphenyl)methylium Ions with Nitranions in Sulfolane/3-Methylsulfolane (5%) at 25 °C

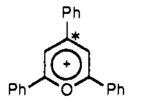


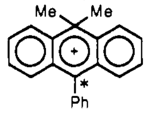


nitranion of	perinaphthenium[a]			bis(4-methoxyphenyl)methylium[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
phthalimide	30.34 ± 0.50	−3.76 ± 0.21	26.58 ± 0.54	32.58 ± 1.19	6.32 ± 0.21	38.90 ± 1.21
succinimide	33.27 ± 0.43	−2.56 ± 0.35	30.71 ± 0.55	34.40 ± 0.78	7.52 ± 0.35	41.92 ± 0.85
3,6-dibromocarbazole	38.98 ± 0.98	−3.39 ± 0.24	35.59 ± 1.01	40.19 ± 1.20	6.69 ± 0.24	46.88 ± 1.22
carbazole	45.30 ± 1.20	−7.82 ± 0.33	37.48 ± 1.24	44.21 ± 0.88	2.26 ± 0.33	46.47 ± 0.94

[a] pK_{R^+} = unknown, $E_{1/2}(C^+) = -0.013 \pm 0.002$ V. [b] $pK_{R^+} = -5.65$, CRP = 18.1, $E_{1/2}(C^+) = -0.450 \pm 0.002$ V.

Table VIII. Heats of Heterolysis, Heats of Homolysis, and Free Energies of Electron Transfer (kcal/mol) for Reactions of Triphenylpyrylium and 9,9-Dimethyl-10-phenyl-9,10-dihydroanthracenium Ions with Nitranions in Sulfolane/3-Methylsulfolane (5%) at 25 °C





nitranion of	triphenylpyrylium[a]			9,9-dimethyl-10-phenyl-9,10-dihydroanthracenium[b]		
	ΔH_{het}	ΔG_{ET}	ΔH_{homo}	ΔH_{het}	ΔG_{ET}	ΔH_{homo}
phthalimide				29.76 ± 0.44	−0.99 ± 0.21	28.77 ± 0.49
succinimide	8.11 ± 0.67	14.90 ± 0.38	23.01 ± 0.77	31.58 ± 0.56		
3,6-dibromocarbazole	15.78 ± 0.99	14.07 ± 0.28	29.85 ± 1.03	36.18 ± 1.23	−0.62 ± 0.24	35.56 ± 1.25
carbazole	24.83 ± 1.29	9.64 ± 0.36	34.47 ± 1.34	41.46 ± 0.71	−5.05 ± 0.33	36.41 ± 0.78

[a] pK_{R^+} = unknown, $E_{1/2}(C^+) = -0.770 \pm 0.007$ V. [b] $pK_{R^+} = -5.49$, CRP = 10.6, $E_{1/2}(C^+) = -0.133 \pm 0.002$ V.

onance-stabilized species which are not complicated by competitive rapid chemical reactions.

Results and Discussion

Tables IV–VIII present our experimental results and derived values for the 36 compounds produced by the reactions of the four nitranions with the nine carbenium ions. Further information concerning the properties of the carbenium ions and their reactions with a series of carbanions and phenoxide and thiophenoxide anions will be found in refs 1–6. Relevant properties for the carbenium ions themselves are presented in each table and are as follows: pK_{R^+} represents the stability of the carbenium ion relative to its carbinol precursor in aqueous sulfuric acid.[19] It is the most widely used parameter for describing carbenium ion stability. A derived property is the carbinol reduction potential (CRP), which is the homolytic bond dissociation energy for the carbinol.[2] Thus, $1.37pK_{R^+}$ is the free energy of heterolytic cleavage of the carbinol precursor of the carbenium ion relative to a standard state of infinite dilution in water. $E_{1/2}(C^+)$ is the reduction potential for the carbenium ion, which, according to Scheme I, is combined with $E_{1/2}$ for the nitranion in order to obtain the standard free energy of electron transfer (ΔG_{ET}) needed to convert the heat of heterolysis (ΔH_{het}) in sulfolane into the corresponding heat of homolysis (ΔH_{homo}).

In Table IV the necessary data for the four nitranions are also presented. Accordingly, the pK_a is related to the free energy of heterolytic dissociation of the nitrogen–hydrogen bond through the familiar expression $\Delta G° = 1.37pK_a$. AOP is the acid oxidation potential of the nitrogen acid, which is related to the homolytic free energy of dissociation of the nitrogen–hydrogen bond through the addition of an appropriate constant.[20]

Although the thermodynamic data do not by themselves automatically provide any structural information, there is every reason to believe, on the basis of our experience with carbon–carbon, carbon–oxygen, and carbon–sulfur bonds,[1–5] that the nitranion reacts at the nitrogen atom from which the acidic hydrogen was detached and that the carbenium ions are attacked at the usual position, from which an appropriate leaving group was removed in order to form the ion. For clarification we have marked this position on each table with a star.

In contrast to our previous studies which involved the series of fluorenyl, phenoxy, and thiophenoxy ions,[1–5] the four nitranions are not related to each other in any structurally systematic way. Nevertheless, in general, the data for the 36 compounds produced by reaction of the nine cations with the four nitranions follow trends that are well-precedented in our previous results for carbon–carbon,[1–3] carbon–oxygen,[4] and carbon–sulfur bonds.[5] By

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(19) Bethel, D.; Gold, V. *Carbonium Ions—An Introduction*; Academic Press: New York, 1967; Chapter 4, p 59.

(20) Bordwell, F. D.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.

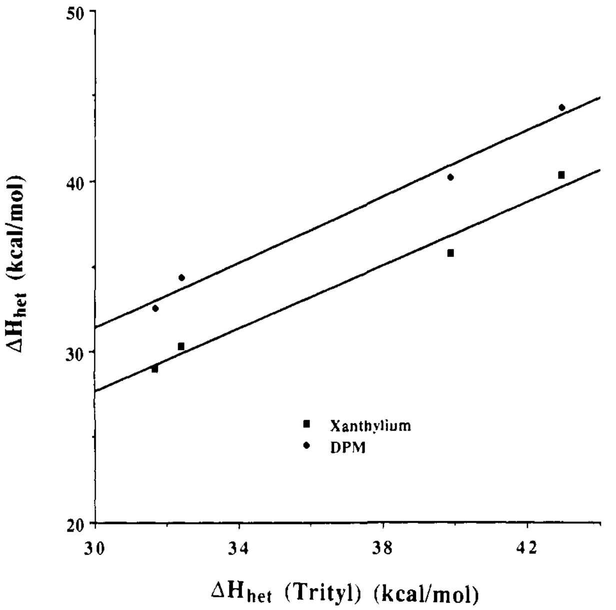

Figure 1. Plots of heats of heterolysis of nitranions with xanthylium and bis(4-methoxyphenyl)methylium ions versus those of nitranions with the triphenylmethylium ion. $\Delta H_{het}(xan^+) = 2.73 + 0.96\Delta H_{het}(trityl^+)$. $R = 0.990$. $\Delta H_{het}(DPM^+) = -0.18 + 0.93\Delta H_{het}(trityl^+)$. $R = 0.997$.

inspection of Table IV, there is a close parallel between the pK_a's of the nitrogen acids and the ΔH_{het}'s for cleavage of the carbon–nitrogen bonds formed by reaction between the anions and carbenium ions. This follows a general pattern of importance to many physical/organic interpretations; namely, the affinities of a series of anions for the proton are proportional to their affinities for a given carbenium ion.

In contrast to our previous results, there is no obvious correlation between the oxidation potentials for the nitranions ($E_{1/2}$'s) and the corresponding pK_a's, albeit a sample data set of four structurally dissimilar compounds is too small for drawing general conclusions. We have already discussed the corresponding relations between pK_{R^+}'s and reduction potentials of carbenium ions. Again, the complete lack of correlation between heterolytic ΔH_{het}'s and homolytic ΔH_{homo}'s is thoroughly precedented in our other studies where we have demonstrated the very general principle that properties which involve the gain or loss of charge correlate closely with each other.[1-5] Correspondingly, properties which do not involve any change of charge correlate well with each other, but there is no correlation between the two different sets of properties.

Finally, the same general sequence of ΔH_{het}'s is observed for the series of nitranions with each carbenium ion, and this is portrayed pictorially in Figure 1, where ΔH_{het}'s for the carbon–nitrogen bonds formed from two other carbenium ions are plotted against those for the trityl cation. Similar plots of ΔH_{het}'s of carbenium ions against ΔH_{hel} for the trityl carbenium ion yield good to poor correlations (for PNA^+, $R = 0.976$; for DPA^+, $R = 0.976$; for 9-PhXa$^+$, $R = 0.963$; for TPP^+, $R = 0.960$; for $C_7H_7^+$, $R = 0.935$; for $TPCP^+$, $R = 0.882$).

Acknowledgment. We wish to express our appreciation to the Gas Research Institute for its generous support of this research and to Professor Vernon Parker for helpful criticisms. E.M.A. is also pleased to express appreciation to Loren Hepler, on the occasion of his retirement, for his patient introduction to and instruction in the science and art of calorimetry during the winter of 1962.

Registry No. $(Ph)_3C^+$, 13948-08-8; phthalimide monoanion, 28627-68-1; succinimide monoanion, 28627-67-0; 3,6-dibromocarbazole monoanion, 79990-92-4; carbazole monoanion, 23560-25-0; 9-phenyl-9-xanthylium, 20460-07-5; 9-xanthylium, 261-23-4; triphenylcyclopropenylium, 12190-17-9; tropylium, 26811-28-9; perinaphthenium, 12147-01-2; bis(4-methoxyphenyl)methylium, 13948-07-7; 2,4,6-triphenylpyrlium, 15959-35-0; 10,10-dimethyl-10-phenyl-9,10-dihydro-9-anthracenylium, 30880-10-5.

Synthesis of Dipeptides by the Photolytic Coupling of Chromium–Aminocarbene Complexes with α-Amino Acid Esters

James R. Miller, Shon R. Pulley, Louis S. Hegedus,* and Stephane DeLombaert

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received December 27, 1991*

Abstract: Photolysis of optically active chromium–aminocarbene complexes in the presence of esters of optically active α-amino acids generates dipeptides in excellent yield and with high diastereoselectivity. In this reaction, both the peptide linkage and the stereogenic center on the carbene-complex-derived amino acid fragment are formed in the same step. The process is subject to double diastereoselection, with the (*S*)(*S*) dipeptide being the matched pair and the (*R*)(*S*) the mismatched pair. Both diastereoisomers can be made with high diastereoselectivity in this reaction.

Introduction

The volume of synthesis of natural and unnatural α-amino acids,[1] and their incorporation into peptides,[2] has experienced explosive growth in the last several years, driven primarily by major advances in the understanding of enzyme mechanisms and the concomitant development of synthetic peptide pharmaceuticals. However the requisite amino acids are synthesized, they are almost invariably incorporated into synthetic peptides by the standard array of classical peptide-coupling techniques, developed over the past 30 years,[3] and undergoing constant refinement even today. Current research in our laboratories has centered on development of photochemical reactions of chromium–aminocarbene complexes[4]

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(1) For reviews see: (a) Williams, R. M. *Synthesis of Optically Active α-Amino Acids*; Baldwin, J. E. Ed.; Pergamon Press: Oxford, U.K., 1989; Organic Chemistry Series, 7. (b) O'Donnell, M. J., Ed. Tetrahedron Symposium in Print, 33, α-Amino Acid Synthesis. *Tetrahedron* **1988**, *44*, 5253–5614.

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