Oxidation of Alkenes with Aqueous Potassium Peroxymonosulfate and No Organic Solvent

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Aqueous potassium peroxymonosulfate oxidizes water-immiscible alkenes at room temperature in the absence of organic solvent. Acidic (pH ≤ 1.7) solutions of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in water produced the epoxide from cyclooctene and diols from all other reactive alkenes investigated. Adjustment of initial pH to ≥ 6.7 with $NaHCO_3$ enabled selective epoxidations of 2,3-dimethyl-2-butene, 1-methylcyclohexene, cyclohexene, styrene, and β-methylstyrene. The order of decreasing reactivity of alkenes was: 2,3-dimethyl-2-butene > 1-methylcyclohexene ≥ cyclohexene > cyclooctene > α-methylstyrene ≥ β-methylstyrene > styrene > p-methylstyrene > allylbenzene. 1-Octene and tetrachloroethylene did not react. Phase-transfer catalysts, a colloidal cationic polymer, and a cationic surfactant microemulsion had little effect on the reaction.

Epoxides are among the most important intermediates in organic synthesis. They are most often prepared from alkenes with organic peroxy acids in homogeneous organic solutions. We have discovered that aqueous potassium peroxymonosulfate oxidizes many alkenes to diols in acidic mixtures and to epoxides in neutral mixtures with no added organic solvent.

Peroxymonosulfuric acid (Caro's acid, H_2SO_5)[1] is a strong oxidant, but is unstable. The stable commercial triple salt, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, is prepared by reaction of 86% H_2O_2 with concentrated H_2SO_4, followed by neutralization with K_2CO_3.[2] By X-ray analyses of $KHSO_5 \cdot H_2O$ and $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, the structure of the peroxymonosulfate anion is $HOOSO_3^-$, with the bond lengths of the three terminal S–O and one internal S–O (peroxo) bonds similar to those in $S_2O_8^{2-}$ and the O–O distance similar to that in H_2O_2.[3]

Like Caro's acid,[4-6] potassium peroxymonosulfate is a powerful oxidant. It oxidizes alcohols, ketones, carboxylic acids, alkenes, arenes, phenols, amines, and sulfides.[7,8] It hydroxylates alkanes and aromatic compounds[9] and delignifies wood.[10] In biphasic mixtures of water, a ketone (usually acetone), dichloromethane, and a phase-transfer catalyst (PTC), $KHSO_5$ epoxidizes alkenes.[11-15] The active oxidant in this system is a dioxirane generated by reaction of $KHSO_5$ with the ketone. Without the ketone no epoxidation occured. The mixtures were buffered at pH 7–8 with phosphate to avoid Bayer–Villiger oxidation of ketones. Epoxidations of alkenes with $KHSO_5$ catalyzed by manganese porphyrins[16,17] and platinum complexes[18] also

Table I. Effect of Stirring Speed on the Yield of Epoxidation[a]

speed, rpm	yield, %	speed, rpm	yield, %
<1000	52	800[c]	70
1800	67[b]	2500	75

[a] All experiments were carried out at 23 °C for 5 h with 0.35 mmol of cyclooctene and 0.16 M (0.37 mmol) $KHSO_5$ in 2.3 mL of aqueous mixture. [b] Average mol % of three runs with a standard deviation ±2%. [c] Mechanical stirring.

Table II. Effects of Amount and Concentration of $KHSO_5$ on Epoxidation[a]

$KHSO_5$, mmol	$KHSO_5$, M	epoxide yield, %
0.44	0.10	84
0.44	0.19	78
0.44	0.22	77
0.44	0.25	73
0.60	0.05	97
0.60	0.13	88
0.60	0.26	83
0.60	0.30	78
0.60	0.61	41

[a] All experiments were carried out with 0.35 mmol of cyclooctene and 1800 rpm magnetic stirring at 23 °C for 5 h.

Table III. Effect of $KHSO_5$ Concentration[a]

$KHSO_5$, M	mol ratio $KHSO_5$/cyclooctene	yield, %
0.16	1.06	65
0.19	1.28	78
0.26	1.70	83
0.39	2.55	80

[a] Reactions were carried out under the conditions of Table II.

have been reported, but are impractical because organometallic complexes decompose rapidly during the epoxidation. Mixtures of water-methanol (or ethanol), or water-ethanol-acetic acid overcome the low solubility of $KHSO_5$ in organic solvents, but the organic solvents are also oxidized, and large excesses of $KHSO_5$ are needed to obtain good yields of epoxides.[7,19] Another problem is that organic-$KHSO_5$ mixtures may cause combustion.[4] We report here a simpler $KHSO_5$ epoxidation method that could be practical for both laboratory and industrial processes.

Results and Discussion

Epoxidation of Cyclooctene. In a vigorously stirred two-phase mixture 1.7 molar equiv of aqueous $KHSO_5$

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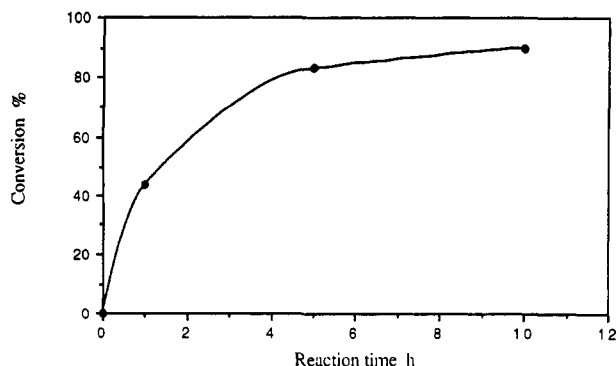(19) Bloch, R.; Abecassis, J.; Hassan, D. *J. Org. Chem.* **1985**, *50*, 1544.

Figure 1. Percent epoxidation of cyclooctene vs time. Conditions were those of Table I except for use of 0.60 mmol of KHSO₅.

epoxidize cyclooctene to >80% epoxide with no significant byproduct in 5 h at room temperature. After 70% conversion, the cyclooctene oxide crystallizes and is isolated easily by filtering the reaction mixture. In a small preparative-scale experiment, 3 g (28 mmol) of cyclooctene and 185 mL of 0.26 M KHSO₅ produced 2.85 g (81%) of cyclooctene oxide.

As expected with two liquid phases, the yield increased with the speed of magnetic stirring of 2.3 mL-scale reaction mixtures as shown in Table I. Yields were reproducible at ≥1800 rpm but not at <1000 rpm. Mechanical stirring also gave a high yield. Magnetic stirring at ≥1800 rpm was used in all subsequent small-scale experiments to ensure high conversion and reproducibility.

Yields of cyclooctene oxide depended upon concentrations of reactants and on the amount of excess KHSO₅ in a surprising way: The yield decreased as the concentration of KHSO₅ increased at each of two different constant molar ratios of KHSO₅ to cyclooctene, as shown in Table II. With constant amounts of cyclooctene and water and varied excess amounts of KHSO₅, a maximum yield was reached using 0.26 M KHSO₅, and the yield declined at higher KHSO₅ concentration as shown in Table III. We hypothesized that the reaction occurs in the aqueous phase and that the lower yields at higher KHSO₅ concentration might be due to lower concentration of cyclooctene in the aqueous phase at high ionic strength. Therefore, we measured the solubilities of cyclooctene at 23 °C in deionized water and in a solution of 0.46 M KHSO₄ and 0.15 M K₂SO₄ (ionic strength = 0.91 M, the same as that of the third entry of Table III) to be 1.7×10^{-4} M and 1.0×10^{-4} M, respectively. We also estimated the solubility of cyclooctene in pure water to be 2×10^{-4} M by extrapolation from literature data on solubilities of related cycloalkanes and cycloalkenes.[20,21] Thus, increasing the KHSO₅ triple salt concentration decreases the cyclooctene concentration, which supports the hypothesis that epoxidation occurs in the aqueous phase.

Figure 1 shows the epoxidation yield as a function of time. More than 90% of the epoxide was produced in the first 5 h. After 10 h about 1% of *trans*-1,2-cyclooctanediol was found also, presumably from ring-opening hydration of the epoxide. In a control experiment using cyclooctene oxide in place of cyclooctene under the usual experimental conditions only unchanged cyclooctene oxide was recovered. Its greater stability than that of other epoxides in the acidic mixture is presumably due to its insolubility.

Often quaternary ammonium salts catalyze biphasic reactions of an organic substrate with an aqueous salt. A

Table IV. Epoxidation of Cyclohexene in the Presence of NaHCO₃[a]

NaHCO₃ mmol	pH before reaction	pH after reaction	cyclohexene, mol %	epoxide, mol %	diol, mol %
0	1.58	1.30	0	0	100
0.50	6.38	2.42	0	0	100
0.60	6.60	4.18	0	30	70
0.65	6.68	7.65	6	90	4
0.70	6.75	8.16	4	95	1
0.80	6.86	8.68	11	88	1
1.0	7.10	8.48	16	83	1

[a] Reactions were performed at 23 °C for 5 h with 0.35 mmol of cyclohexene and 0.44 mmol (0.19 M) of KHSO₅ in 2.3 mL of aqueous mixture.

phase-transfer catalyst (18-crown-6 ether or tetrabutylammonium hydrogen sulfate) is necessary in the biphasic epoxidations with ketones and KHSO₅.[11-14] However, the common phase-transfer catalysts tetrabutylammonium hydrogen sulfate, benzyltriethylammonium chloride, and Aliquat 336 had little effect on our KHSO₅ epoxidation of cyclooctene. Recent successes with cationic polymer colloids for catalysis of epoxidations in similar liquid–liquid mixtures[22] prompted us to try as catalysts colloidal polystyrene particles containing 23 mol % of benzyltrimethylammonium chloride repeat units and a cationic surfactant microemulsion containing 1-octadecanol and hexadecyltrimethylammonium bromide, but they too had little effect on the rate of epoxidation of cyclooctene. We conclude that the epoxidation occurs in the aqueous phase and that the phase-transfer catalysts and microemulsion components have little effect on the cyclooctene concentration in the aquous phase. In support of this conclusion, we measured the solubility of cyclooctene in a solution of 0.46 M KHSO₄, 0.15 M K₂SO₄, and 0.0030 M benzyltriethylammonium chloride (BTAC) to be 1.0×10^{-4} M, the same as in the absence of BTAC.

Epoxidation of Cyclohexene. At the pH 1.6 used to epoxidize cyclooctene, diols were produced from all other alkenes studied, presumably by acid-catalyzed addition of water to the epoxide. In a control experiment using cyclohexene oxide in place of cyclohexene under identical conditions, the epoxide was converted completely to *trans*-1,2-cyclohexanediol. To obtain epoxides from other alkenes, the pH of the aqueous phase was adjusted to nearly neutral using sodium bicarbonate. Results of oxidations of cyclohexene with KHSO₅ in Table IV indicate that the only product was diol if the initial pH was below 6.38, and 99% of products was cyclohexene oxide at pH ≥ 6.75. With NaHCO₃ at pH 7.1, the conversion of cyclohexene decreased, probably due to a higher decomposition rate of KHSO₅. Ball and Edwards[5] found that the second-order rate constant of decomposition of Caro's acid in phosphate buffer solution doubled when pH increased from 6.7 to 7.1. KHSO₅ is relatively stable at pH <6 and at pH 12, and it decomposes fastest at pH 9.4. (The pK_a of HSO₅⁻ is 9.4 at 25 °C in water).[5,6] In the absence of alkene only 19% of active KHSO₅ remained after stirring the KHSO₅ solution of initial pH 6.75 and final pH 6.85 at 23 °C for 5 h. After a 5-h oxidation of cyclohexene at initial pH 6.75, none of the initial excess of KHSO₅ was detected by iodometric titration. Thus, epoxidation and HSO₅⁻ self-decomposition occur simultaneously in the aqueous phase. The epoxidation is favored in the presence of organic substrates and at lower KHSO₅ concentration

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Table V. Oxidations of Alkenes at pH ≤1.68[a]

alkene	temp, °C	initial pH	final pH	alkene, mol %	epoxide, mol %	diol, mol %	solubility,[b] M × 10[4]
2,3-dimethyl-2-butene[c]	23	1.56	1.46	0	0	100	2.9[d]
2,3-dimethyl-2-butene[e]	23	1.68	1.32	11	0	89	
1-methylcyclohexene[c]	23	1.56	1.48	0	0	100	5.4[e]
1-methylcyclohexene[e]	23	1.68	1.35	26	0	74	
cyclohexene[c]	23	1.56	1.32	0	0	100	26[f]
cyclohexene[e]	23	1.68	1.40	51	0	49	
cyclooctene	23	1.58	1.30	22	78	0	1.7
α-methylstyrene	23	1.58	1.40	43	1	56	1.7[g]
α-methylstyrene[h]	23	1.58	1.40	23	6	66	
α-methylstyrene	40	1.58	1.40	0	5	95	
β-methylstyrene	23	1.58	1.40	65	0	35	1.7[g]
β-methylstyrene	40	1.58	1.30	3	7	90	
styrene	23	1.58	1.40	76	0	24	7.0[i]
styrene	40	1.58	1.20	23	0	77	
p-methylstyrene	23	1.58	1.60	95	0	5	1.7[g]
p-methylstyrene	40	1.58	1.30	29	0	68	
allylbenzene	23	1.58	1.70	98	2	0	1.7[g]
allylbenzene	50	1.58	1.30	70	0	30	
1-octene	23	1.58	1.70	100	0	0	0.24[f]
1-octene[j]	23	1.58	1.60	98	0	2	
1-octene	50	1.58	1.62	99	0	1	
tetrachloroethylene	23	1.56	1.80	100	0	0	9.0[k]

[a] Conditions were the same as in Table IV line 1 unless noted otherwise. [b] Solubility of alkene in water at 23 °C. Estimates are from literature values of homologues and an assumed decrease of solubility by a factor of 0.25 per additional CH_2 group.[21] [c] 0.70 mmol of alkenes and 0.88 mmol of $KHSO_5$ in 4.6 mL of aqueous phase at 23 °C for 1 h. [d] Estimated from 2-methylpropene.[20] [e] 0.70 mmol of alkenes and 0.70 mmol of $KHSO_5$ in 4.6 mL of aqueous phase for 30 min. [f] Reference 20. [g] Estimated from styrene.[23] [h] Carried out in the presence of 20 mg of a cationic polystyrene colloid. [i] Reference 23. [j] 24 h reaction time. [k] Reference 24.

Table VI. Oxidations of Alkenes at pH >6.6[a]

alkene	temp, °C	initial pH	final pH	alkene, mol %	epoxide, mol %	diol, mol %
2,3-dimethyl-2-butene[b]	23	6.68	8.20	0	98	2
2,3-dimethyl-2-butene[c]	23	6.68	8.32	12	88	0
1-methylcyclohexene[b]	23	6.68	7.60	9	91	0
1-methylcyclohexene[c]	23	6.68	7.76	40	60	0
cyclohexene[c]	23	6.68	7.92	38	62	0
cyclohexene	23	6.75	8.16	1	95	0
α-methylstyrene	23	6.70	7.20	82	13	5
α-methylstyrene	40	6.70	6.75	85	3	12
α-methylstyrene[d]	23	6.80	7.60	30	18	49
α-methylstyrene[e]	23	7.05	7.18	44	33	22
β-methylstyrene	23	6.70	6.70	63	37	0
β-methylstyrene	40	6.70	8.30	63	37	0
β-methylstyrene[d]	23	6.80	7.56	21	79	0
styrene[d]	23	6.80	7.70	56	44	0
styrene	40	6.70	7.10	84	12	4
tetrachloroethylene	23	6.68	7.80	100	0	0

[a] Conditions were the same as in Table IV unless noted otherwise. [b] 0.70 mmol of alkenes and 0.88 mmol of $KHSO_5$ in 4.6 mL of aqueous phase at 23 °C for 1 h. [c] 0.70 mmol of alkenes and 0.70 mmol of $KHSO_5$ in 4.6 mL of aqueous phase for 30 min. [d] 0.60 mmol of $KHSO_5$ (0.05 M) and 0.87 mmol of $NaHCO_3$ (0.07 M) in 12 mL of aqueous mixture. [e] 1.4 mmol of alkene, 2.40 mmol of $KHSO_5$ (0.05 M), and 4.08 mmol of $NaHCO_3$ (0.085 M) in 48 mL of aqueous mixture.

due to the second-order self-decomposition kinetics. Although the amounts of $NaHCO_3$ used for epoxidations were not enough to maintain constant pH throughout the reaction, the $NaHCO_3$ did prevent the ring opening of cyclohexene oxide. The $NaHCO_3$ buffering method could be applied to other reactions in which approximate control of pH is required.

Oxidations of Other Alkenes. At initial pH 1.6, $KHSO_5$ oxidations of 2,3-dimethyl-2-butene, 1-methylcyclohexene, allylbenzene, and styrene derivatives produced diols as shown in Table V. 2,3-Dimethyl-2,3-butanediol was stable at pH 1.5 and did not undergo pinacol rearrangement. At initial pH > 6.6, $KHSO_5$ produced epoxides in good yields from 2,3-dimethyl-2-butene and 1-methylcyclohexene under the standard conditions, but lower yields from the other alkenes as shown in Table VI. Increase of temperature from 23 to 40 °C under neutral conditions did not raise the yields of epoxidation, possibly due to faster decomposition of the oxidant. Higher conversions to diols were observed at 40 °C and pH ≤ 1.7.

1-Octene was only 2% oxidized after 24 h. Tetrachloroethylene did not react under either acidic or neutral conditions. As with cyclooctene, dilution of the $KHSO_5$ at neutral pH gave higher yields of epoxides: 79% of β-methylstyrene oxide and 44% of styrene oxide (see Table VI).

Use of more $NaHCO_3$ to attain higher pH (6.80 vs 7.05) of the aqueous phase nearly doubled the yield of α-methylstyrene oxide (18% to 33%), but gave lower alkene conversion. More $NaHCO_3$ favors production of the epoxide, but decreases the solubility of the alkene in aqueous phase because of the high ionic strength. Epoxidation of β-methylstyrene (cis/trans = 8/92) at pH 6.8 gave a 10/90 mixture of cis- and trans-β-methylstyrene oxides in 79% yield. This suggests but does not prove that the epoxidation is stereospecific. Oxidation of the same mixture of β-methylstyrenes at pH 1.58 produced erythro- and threo-1-phenyl-1,2-propanediol in equal amounts.

Mechanism of Epoxidation. A probable mechanism for the epoxidations is transfer of the electrophilic per-

hydroxyl oxygen atom of $KHSO_5$ to the alkene (eq 1),
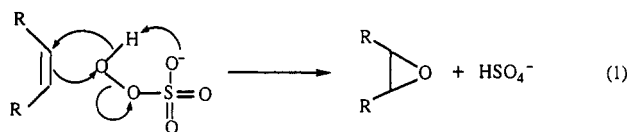
similar to the mechanism of epoxidation of alkenes by organic peroxy acids. The production of $KHSO_4$ (pK_a 1.9) from $KHSO_5$ (pK_a 9.4) causes the decrease of pH from 1.58 to 1.30 usually observed during the oxidations in the absence of $NaHCO_3$ (see Table V).

After excess $NaHCO_3$ solution is added to pH > 6.6, the reaction mixture is buffered if CO_2 does not evolve (eq 2)

$$HSO_4^- + HCO_3^- \rightarrow H_2CO_3 \rightarrow H_2O + CO_2\uparrow \quad (2)$$

because of the presence of sizeable amounts of both HCO_3^- and H_2CO_3. The pH of this solution follows eq 3:

$$pH = 6.37 + \log ([HCO_3^-]/[H_2CO_3]) \quad (3)$$

Thus, the initial pH is nearly neutral even when $NaHCO_3$ is an excess. As the epoxidation proceeds, the generated $KHSO_4$ is neutralized by the remaining $NaHCO_3$. If we assume that the CO_2 produced from $NaHCO_3$ and $KHSO_4$ evaporates from the solution during the reaction, equilibrium calculations predict approximately the final pH values of all of the reaction mixtures in Table IV.[25] If the amount of $NaHCO_3$ added is less than the amount of $[KHSO_4 + KHSO_5]$, the solution becomes acidic as HSO_4^- is formed. If the amount of $NaHCO_3$ added is greater than the amount of $[KHSO_4 + KHSO_5]$ and CO_2 evaporates, the solution becomes basic due to loss of acid as CO_2.

The buffering action of bicarbonate near neutral pH is similar to the buffering of blood.[26] Acidic metabolites, mainly CO_2, are produced in greater quantities than basic metabolites. The control of CO_2 by pH in blood is maintained by several buffer systems, including bicarbonate and $H_2PO_4^-/HPO_4^{2-}$.

In acidic $KHSO_5$ solution, the reactivity order is 2,3-dimethyl-2-butene > 1-methylcyclohexene > cyclohexene > cyclooctene > α-methylstyrene > β-methylstyrene > styrene > p-methylstyrene > allylbenzene > 1-octene. In neutral solutions (pH > 6.6), the reactivity order differs only by cyclohexene = 1-methylcyclohexene and β-methylstyrene > α-methylstyrene. The relative rates of oxidation by $KHSO_5$ are similar but not identical to those by electrophilic peroxy acids, increasing with electron-donating methyl groups on the double bond. Relative rates of epoxidation by peroxyacetic acid in acetic acid are 2-methyl-2-butene > cyclopentene > cyclohexene > β-methylstyrene > styrene > allylbenzene.[27]

Solubilities of the alkenes in water could also be a factor in the $KHSO_5$ reactions. Literature and estimated values of the solubilities are given in Table V. Solubilities of hydrocarbons in water decrease by about a factor of four for each additional CH_2 group.[21] Thus the reactivities of α-methylstyrene, β-methylstyrene, and p-methylstyrene may all be reduced relative to that of styrene by lower solubility.

The two-phase $KHSO_5$ epoxidations are compared with other methods in Table VII. The conditions are simple and involve no organic solvent, requiring only alkene,

Table VII. Comparisons of Epoxidations

alkene	$KHSO_5$, equiv	% conv of alkene	% epoxide[a]	ref
cyclohexene	2.4	97	80	11[b]
cyclohexene	1.26	96	99	this work
cyclooctene	1.5		94	19[c]
cyclooctene	1.7	97	100	this work
β-methylstyrene			85	14[b]
β-methylstyrene	1.7	79	100	this work

[a] Epoxide yields are based on alkene reacted. [b] 5.1 mmol of alkene, 12 mmol of $KHSO_5$, and 1 mmol of $Bu_4N^+HSO_4^-$ in 50 mL of CH_2Cl_2, 50 mL of water, and 4 mL of acetone at pH 7.5 buffered by phosphate and by controlled addition of KOH at 2–10 °C for 4 h. [c] 10 mmol of alkene and 15 mmol of $KHSO_5$ in 20 mL of methanol and 20 mL of water at room temperature for 4 h.

$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, $NaHCO_3$, and water. Other methods of $KHSO_5$ epoxidation require organic solvents such as acetone, methanol, and CH_2Cl_2, sometimes phase-transfer catalysts, and continuous addition of KOH. The two-phase procedures might be developed for large-scale production of epoxides and diols.

Experimental Section

GLC analyses were performed on a 6 ft × $^1/_8$ in. Tenax packed column from Supelco Inc. and a thermal conductivity detector using internal standards and response factor calibrations. Controlled magnetic stirring speed experiments were performed with a VWR Scientific 400 HPS instrument that allowed precise control from 0 to 2500 rpm. pH of reaction mixtures was measured with a semimicro combination glass electrode calibrated at pH 2, 7, and 10. Commercial alkenes were used as received. Potassium peroxymonosulfate (DuPont Oxone) was used as received from Aldrich Chemical Co. The material safety data sheet warns that it forms explosive mixtures with as little as 1% organic matter and decomposes on contact with heavy metal salts with the evolution of oxygen. Iodometric titration showed that 1 g of Oxone contained 2.75 mmol $KHSO_5$.[28] A solution of 0.0101 g of Oxone and 10 mL of water had pH 2.93. The solution contained 0.0042 g or 2.77×10^{-3} M of $KHSO_5$ and 0.0059 g of $[KHSO_4 + K_2SO_4]$. From $pK_a(2)$ of $KHSO_4 = 1.92$, equilibrium calculation shows that the above solution contained 0.0022 g (1.60×10^{-3} M) of $KHSO_4$ and 0.0037 g (2.14×10^{-3} M) of K_2SO_4. Thus, the analyzed molar ratio of $KHSO_5/KHSO_4/K_2SO_4$ in Oxone was 1.73:1.0:1.34.

Epoxidation of Cyclooctene. Method 1. A mixture of deionized water (1.57 mL), cyclooctene (0.35 mmol, 46 μL), and freshly prepared Oxone solution (0.73 mL, 0.44 mmol $KHSO_5$) was stirred magnetically at 1800 rpm for 5 h at 23 °C. The mixture was extracted with ethyl ether five times (total volume 6 mL). The extract was dried over Na_2SO_4 and analyzed by GLC using n-octane as an internal standard. GLC analyses accounted for 90–100% of the starting cyclooctene in all experiments.

Method 2. A 500-mL flask was charged with 185 mL of deionized water and 17.2 g of Oxone (48 mmol of $KHSO_5$). The solution was allowed to warm to 23 °C. Cyclooctene (3.09 g, 28 mmol) was added, and the mixture was stirred mechanically at 23 °C for 5 h. The colorless crystals suspended in the aqueous phase were collected by suction filtration (1.80 g, 51%) and analyzed to contain >98.5% cyclooctene oxide and <1.5% cyclooctene. The filtrate was extracted with CH_2Cl_2 (5 × 70 mL). The extract was dried and evaporated to give 1.09 g of colorless crystals containing 96.5/3.5 (w/w) cyclooctene oxide/$trans$-1,2-cyclooctanediol. The total isolated epoxide yield was 2.85 g (81%).

Oxidations of Other Alkenes. The procedure of method 1 was employed except that cyclohexene or other alkenes (0.35 mmol) and $NaHCO_3$ (0.65 mL of freshly prepared 1.0 M solution) were used. In most experiments the order of addition to the flask was water, $NaHCO_3$ solution, alkene, and $KHSO_5$ solution within a period of less than 1 min. In some cases $KHSO_5$ was added before $NaHCO_3$. The pH measurements were made on solutions of $NaHCO_3$ and $KHSO_5$ separately prepared from the same stock

(25) To be reported in the Ph. D. dissertation of Weiming Zhu.
(26) Weinberg, M. S., Sheffner, A. L., Eds. *Buffers in Ruminant Physiology and Metabolism*; Church & Dwight: New York, 1976; p 32.
(27) Swern, D. *Organic Peroxides*; Wiley-Interscience: New York, 1971; Vol. II, Chapter V, p 452.

(28) Vogel, A. I. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman: New York, 1989; pp 390–397.

solutions but lacking the alkene. The combined ether extracts were analyzed by GLC. All of the epoxides and diols were known compounds, and their IR, 300- or 400-MHz ¹H NMR, and 75.4-MHz ¹³C NMR spectral data[25] were identical with those given in the literature or with those of commercial samples.

Control Experiments on Stability of KHSO₅. Iodometric titrations of reaction mixtures immediately after epoxidations of cyclohexene and of cyclooctene at initial pH 1.58 and of cyclohexene at initial pH 6.75 showed that all of the excess oxidant remained after 5 h of reaction under acidic conditions and all of the excess oxidant disappeared after 5 h of reaction under neutral conditions.

Gas-Phase Reactivities and Interchromophoric Effects in 1,*n*-Dicarbazolylalkane Cations and Related Species[†]

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The behavior of gaseous cations derived from electron ionization (20 and 70 eV) and methane chemical ionization (CI) of 1,*n*-dicarbazolylalkanes **1a–5a** (where *n* = 1–5 methylene units, respectively) and the corresponding 3-nitro derivatives **1b–5b** was examined using mass spectrometry. An iminium ion (*m/z* 180) is the major fragment from all 1–5 examined with the exception of **4a**, for which CI affords predominantly a pyrrolidinium ion (*m/z* 222) by displacement of carbazole. Compounds **1a** and **1b** exhibit little [M]•⁺ and [M + H]⁺ and undergo the most extensive fragmentation. Ethylated iminium ion (*m/z* 208) is observed from both **1a** and **1b** under CI conditions, indicating operation of an interannular hydrogen shift. Compound **3a** fragments least, consistent with an exceptional, although small, stabilization for the parent ions of this derivative.

Introduction

The interaction of aromatic rings is one of a number of intermolecular attractive forces[1–7] which can influence molecular structure[5–7] and determine the course of chemical reactions.[8,9] Evidence has been presented for stabilization of arene dimers with stacked[10,11] and "T-shaped"[12,13] configurations. Association is even more favorable for radical cations of aromatic hydrocarbons than for neutral arenes.[14,16] Aggregation affects chemical behavior; for example, radical cations of arene dimers react with nucleophiles and radical species significantly more slowly than do the corresponding monomers.[17,18]

In this regard, we have investigated the crystal structures and reactivities in solution of dicarbazolylalkanes 1–5 (Scheme I) in which two carbazole rings are linked at nitrogen by a polymethylene spacer of varying length.[7,18,19] The number of methylene carbons in these dicarbazole derivatives (being one to five for 1–5, respectively) restricts the geometries for intramolecular interaction between the two terminal carbazole groups. Therefore, interchromophoric interactions can be seen as a function of the length of the saturated chain linking the carbazoles. The nature of such interactions, in turn, influences the delocalization of charge and spin upon oxidation of 1–5 to the respective radical cations [M]•⁺.[20]

Specifically, interaction between two carbazole rings was found to be stabilizing for [M]•⁺ of **3a**, in which "sandwich"

Scheme I
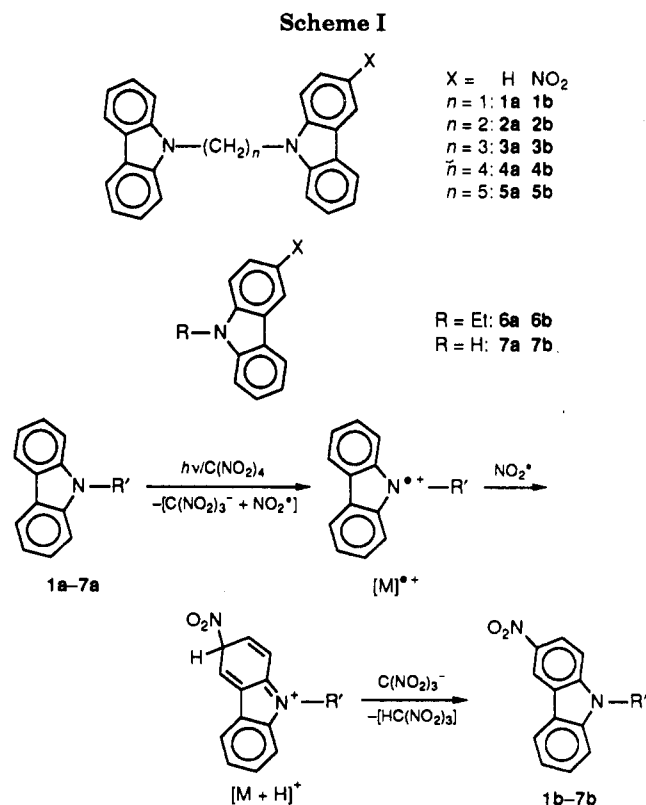
or parallel planar overlap is possible (I) and charge is delocalized between both carbazole rings.[21] Only a small