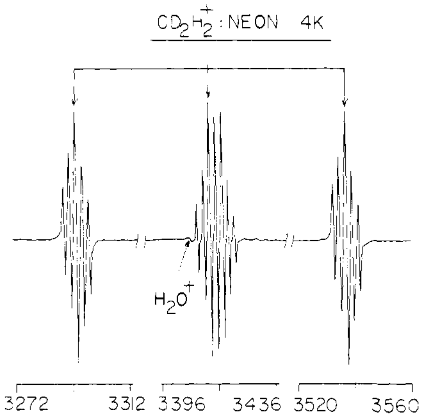

Figure 1. ESR spectrum of $CD_2H_2^+$ isolated in neon matrix at 4 K is shown. The vertical expansion is 4 times greater for the wing quintets relative to the central region. The lowest field component of the background impurity species, H_2O^+ is indicated. Other, very weak lines result from CD_2H and CH_2D radicals. The magnetic field position of g_e occurs at 3421.2 G.

Cd^+.[18] A neon matrix is apparently the only inert medium that can trap small cations having electron affinities greater than approximately 11-12 eV.[15] The large ionization energy of neon (21 eV) is presumably its distinguishing characteristic.

Electron loss from the 3-fold degenerate t_2 orbital of CH_4 can lead to C_{2v}, D_{2d}, and C_{3v} Jahn-Teller-type distortions.[8,10,19] Second-order analysis of the nearly isotropic triplet of quintets ESR spectrum observed for $CD_2H_2^+$ (Figure 1) yields $g_{iso} = 2.0029$ (4), $|A_{iso}(H)| = 121.7$ (3) G, and $|A_{iso}(D)| = 2.22$ (6) G. Multiplication of the D hfs by the appropriate nuclear g factor ratio yields 14.6 (4) G on the H "scale". The quintets result from two equivalent deuteriums ($I = 1$) and the triplet from two equivalent hydrogens. As expected second-order effects of such a large triplet splitting produce two transitions in the central spectral region which appear as partially overlapping quintets. The observation of two groups of two highly inequivalent H-atom positions is consistent only with a C_{2v} assignment. A recent ESR study of BH_4, isoelectronic with CH_4^+, has also reported a C_{2v} structure with $|A_{iso}(H)|$ values of 122 (18) and 10 (11) G.[14]

Ab initio CI spin-density calculations (ref 20 for details) were conducted at the 6-31G* basis set UHF C_{2v} and D_{2d} geometries listed by Pople.[9] For C_{2v}, the two hydrogens in the nodal plane ($\angle HCH = 123°$; C-H = 1.075 Å) of the carbon p orbital containing unpaired electron density had $A = -17$ G; the other two hydrogens ($\angle HCH = 59°$; C-H = 1.164 Å) which are allowed by symmetry to mix with this p orbital had $A = 137$ G. The D_{2d} state, calculated to be only ≈ 900 cm^{-1} above C_{2v}, has four equivalent hydrogens with a theoretical A value of 82 G. The excellent agreement between these theoretical and experimental hfs results further confirms the C_{2v} assignment.

In planar CH_3, all H atoms are in the nodal plane of the carbon 2p orbital containing practically 100% of the unpaired electron and have $A_{iso} = -23.2$ G arising from well-established spin-polarization effects. The small negative deuterium A value for $CD_2H_2^+$, which probably results from a similar spin-polarization mechanism, indicates by a simple ratio estimate that 62% of the spin density resides in the carbon 2p orbital. The two hydrogens with the large positive hfs account for roughly 48% of the spin density thus leaving $\approx 52\%$ in the 2p orbital. This rather crude "difference" estimate shows reasonable agreement with the spin-polarization prediction.

The ESR spectrum of CH_4^+ is an approximately isotropic quintet with $|A_{iso}(H)| = 54.8$ (2) G and $g_{iso} = 2.0029$ (3). It is definitely not a triplet of triplets as would be expected on the basis of $CD_2H_2^+$ results. It is extremely interesting that the weighted average $((2(121.7) - 2(14.6))/4)$ of the $CD_2H_2^+$ A values yield 53.6 G, which is essentially that observed for CH_4^+. Dynamic Jahn-Teller or fluxional behavior could cause rapid averaging of the H environments in CH_4^+. Simple rotational effects alone cannot account for this observation. Presumably, zero point energy differences in $CD_2H_2^+$ prevent such averaging effects at 4 K. Additional theoretical studies are required to explain why the D nuclei prefer the nodal plane positions which according to theory have the shorter bond distance.

Other properties of this important cation radical currently being investigated include ^{13}C hfs, all other deuterated combinations, temperature dependence, preferential orientation effects, a detailed line-shape analysis, and a theoretical treatment of the H/D isotope behavior. Attempts to produce narrower lines for resolution of small anisotropic effects are in progress. Hopefully vibrational studies of CH_4^+ will be conducted by other investigators.

Acknowledgment. NSF support (CHE-8207327) and a Charles H. Townes grant administered by Research Corporation is gratefully acknowledged.

Registry No. Methane cation radical, 20741-88-2; methane-d_2 cation radical, 61105-67-7.

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Reaction of Sydnones with Ozone as a Method of Deamination: On the Mechanism of Inhibition of Monoamine Oxidase by Sydnones

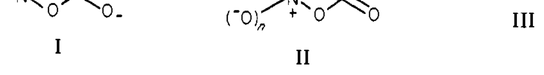
Emil H. White* and Notker Egger

Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland 21218

Received January 27, 1984

Deaminatively produced carbonium ions are intermediates of high reactivity,[1,2] and they have been utilized for this reason in several methods for the inhibition of enzymes.[3,4] We show herein that such ions can be generated by the reaction of sydnones with ozone.

The oxidation of sydnones (I) generally leads to mixtures of degradation products.[5-8] With oxygen gas as the oxidant (13-21-day reaction period), α-ketoacetate esters (8-30%) were found among the reaction products by Nakajima and Anselme.[8] A reasonable pathway for this conversion involves "diazo" ester intermediates[8] (II, $n = 0$, 1), characteristic of deamination reactions[9,10] (eq 1). We have found, in fact, that benzyldiazoic pyruvic anhydride (IV) (generated from the corresponding ni-



I II III (1)

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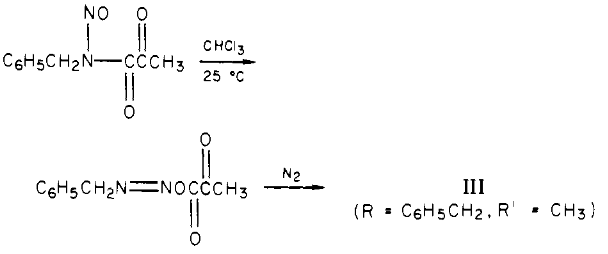
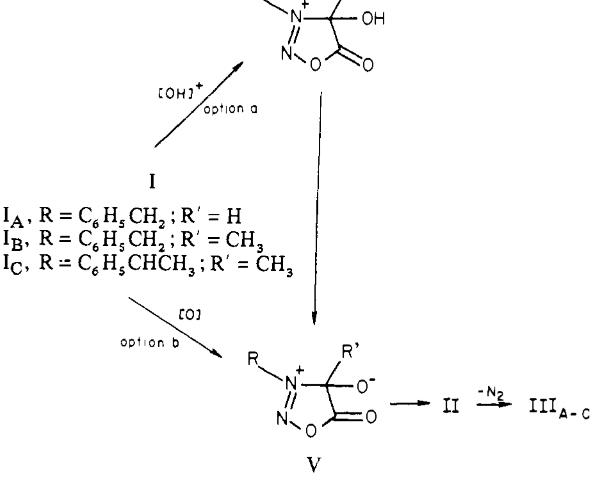
trosoamide) yields benzyl pyruvate quantitatively (eq 2).[11]



$$C_6H_5CH_2N(NO)COCOCH_3 \xrightarrow[25\ ^\circ C]{CHCl_3} C_6H_5CH_2N{=}NOCOCOCH_3 \xrightarrow{N_2} \text{III}\ (R = C_6H_5CH_2,\ R' = CH_3) \quad (2)$$

IV

To favor the deamination route in the oxidation of the sydnones,[14] we have tested reagents that deliver OH^+ or OR^+ groups (in a formal sense) (eq 3a). *meta*-Chloroperbenzoic acid[15] (with I_{A+B}) and chromic anhydride,[16] pyridinium dichromate,[17] and a peroxomolybdenum (VI) complex[18] (with I_B) did produce pyruvate esters (up to 25%), but they were contaminated with the corresponding acetate esters.



I

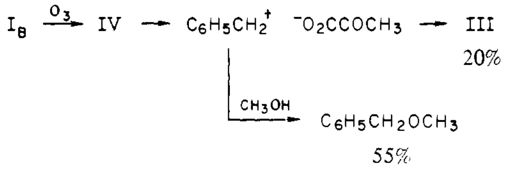
I_A, $R = C_6H_5CH_2$; $R' = H$
I_B, $R = C_6H_5CH_2$; $R' = CH_3$
I_C, $R = C_6H_5CHCH_3$; $R' = CH_3$

V

(3)

The direct conversion of I → V requires the donation of an oxygen atom to the sydnone (eq 3, option b). The reagent ozone acts as an oxygen atom donor in certain of its reactions (with amines and phosphines, for example).[19] We have found that the reaction of sydnones with ozone produces good yields of the pyruvate esters. For example, treatment of 3-benzyl-4-methylsydnone (I_B) in methylene chloride with 1 mol of ozone[20] at −78 °C (or passing in ozone until a blue color appears) affords benzyl pyruvate in yields of 60%.[21]

The sydnone–ozone reactions involve intermediates which react in a manner characteristic of deaminatively formed carbonium ion–carboxylate ion pairs. Thus, interception of the carbonium ion[10] occurs in the presence of methanol (eq 4).[9,22] Further, the reaction of chiral I_C (*S* configuration[23]) yields 1-phenylethyl pyruvate (III_C) with *retention* of configuration;[24] the enantiomeric excess (76%) is essentially the same as that observed in 1-phenylethyl esters from various deamination reactions (eq 5, for example). Sydnones can thus serve as useful precursors of diazonium ion pairs and deaminatively formed carbonium ions.



$$I_B \xrightarrow{O_3} \text{IV} \rightarrow C_6H_5CH_2^+\ {}^-O_2CCOCH_3 \rightarrow \text{III}\ (20\%)$$
$$C_6H_5CH_2^+\ {}^-O_2CCOCH_3 \xrightarrow{CH_3OH} C_6H_5CH_2OCH_3\ (55\%)$$

$$C_6H_5CH(CH_3)N(NO)COC_{10}H_7 \xrightarrow{CH_2Cl_2} C_6H_5CHCH_3N{=}NOCOC_{10}H_7 \rightarrow C_6H_5CHCH_3OCOC_{10}H_7 \ \text{(68\% retn of config)} \quad (5)$$

As a model for the sydnone oxidation, we also examined the reaction of a carbanion with ozone (eq 6). The anion of diethyl methylmalonate gave the corresponding hydroxyl compound (VI)[27] in good yield. We have been able to find only two other instances

$$CH_3CH(COOC_2H_5)_2 \xrightarrow[(2)\ O_3,\ CH_2Cl_2,\ -78\ ^\circ C]{(1)\ NaH,\ THF} \underset{\text{VI}}{CH_3CH(OH)(COOC_2H_5)_2} \quad (6)$$

of the reaction of a carbanion with ozone: nitronate ions with ozone yield the corresponding carbonyl compounds and nitrate ion[28] and nitrones yield carbonyl and nitroso compounds.[29,30] In view of the ease of performing these reactions, oxygen atom transfer from ozone to carbanions would appear to be a useful synthetic reaction.

Sydnones have been reported to be inhibitors of the enzyme monoamine oxidase.[31] The results reported above provide a rational basis for the inhibition since we have shown that deaminatively formed carbonium ions can be potent inhibitors of enzymes. In the case of chymotrypsin, deaminatively formed benzyl cations inhibit[3,32,33] the enzyme through alkylation of functional

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[11] Intermediates such as II ($n = 1$) and IV yield N_2O and N_2, respectively, but otherwise identical products.[12,13]

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[14] Sydnones I_{A-C} were prepared by dehydration of the corresponding α-nitrosoamino acids (Baker, W.; Ollis, W. D.; Poole, V. D. *J. Chem. Soc.* **1949**, 307). Sydnone I_A, mp 66–67 °C, had been previously reported by Baker et al. Sydnone I_B had been reported but not characterized (Padwa, A.; Burgess, E. M.; Gingrich, H. A.; Roush, D. M. *J. Org. Chem.* **1982**, *47*, 786); we find mp 54–57 °C. For sydnone I_C (prepared from (*S*)-1-phenylethylamine), mp 121–123 °C (sealed, evacuated capillary): UV (C_2H_5OH) 299 nm (ε 7700); IR (KBr) 1772, 1730 (sh), 1710, 1440, 1234 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 7.5–7.1 (m, 5 H), 5.53 (q, $J = 7$ Hz, 1 H), 1.98 (d, $J = 7$ Hz, 3 H), 1.92 (s, 3 H); $[\alpha]^{25}_D$ +30.79° (c 2.66, $CHCl_3$). The sydnones and pyruvate esters gave elemental analyses and physical data consistent with the assigned structures [the pyruvate esters were prepared by the method of R. W. Binkley (*Synth. Commun.* **1976**, *6*, 281)].

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[21] Benzyl alcohol, benzyl acetate, *N*-benzyl-*N*-nitrosoacetamide, and pyruvic acid are minor products (formed directly at −40 °C and detected by NMR); they can be readily removed by passage over silica gel. The yields of these byproducts becomes still less in ozone–sydnone reactions carried out at −100 °C.

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[23] (−)-1-Phenylethylamine and (−)-1-phenylethanol have the *S* configuration (Klyne, W.; Buckingham, J. "Atlas of Stereochemistry", 2nd ed.; Oxford University Press: New York, 1978; Vol. I. For (*S*)-1-phenylethyl pyruvate we find $[\alpha]^{25}_D$ −69.9° (c 2.95, benzene).

[24] Retention of configuration is the rule for intramolecular deamination reactions in the absence of neighboring group interactions.[9,10]

[25] Similar stereochemical results have been reported in other studies.[9,10,13,26]

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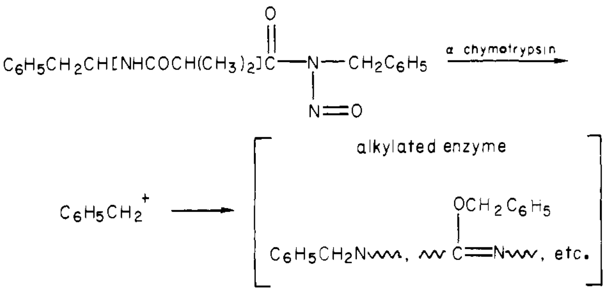
groups and also through alkylation of the amide linkages[34] (eq 7). The sydnone[35,36] and nitrosoamide cases would appear to be related examples of enzyme-activated substrate inhibition.[32,36–38]



Acknowledgment. This research was supported by Grant 19488 from the Institute of General Medical Sciences of the U.S. Public Health Service. We thank Dr. D. F. Roswell for preliminary investigations of the sydnones.

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[33] Similar results have been obtained with several nitroso lactams,[32] which, in addition, have been found to inhibit trypsin, elastase, and subtilisin BPN′ (research of Dr. Douglas Hayes).

[34] Reference 32 and unpublished work of Dr. Stephano Donadio.

[35] The enzyme-moderated oxidation of sydnones may involve two one-electron transfers (Silverman, R. B.; Yamasaki, R. B. *Biochemistry* **1984**, *23*, 1322–1333.

[36] We thank Dr. Silverman for preprints of ref 35 and 37.

[37] Silverman, R. B.; Hoffman, S. J. *Med. Res. Rev.*, in press.

[38] Also called mechanism based and suicide inhibition (Colowick, S. P.; Kaplan, N. O. *Methods Enzymol.* **1977**, *46*. Kalman, T. I. "Drug Action and Design"; Elsevier/North-Holland: New York, 1979; Vol 6.

Secondary Deuterium Kinetic Isotope Effect in S_E2 Replacement Reactions[1a]

Dante J. Bencivengo, Marilyn L. Brownawell,
Ming-Yang Li,[1b] and Joseph San Filippo, Jr.*

Department of Chemistry
Rutgers, The State University
New Brunswick, New Jersey 08903

Received February 3, 1984
Revised Manuscript Received April 30, 1984

In principle, the utility of the hydrogen secondary kinetic isotope effect for investigating S_E2 transition states could be as great as it has been for S_N1 and S_N2 reactions at saturated carbon.[2–4] Here we report the first such determinations associated with bimolecular electrophilic substitution reactions.

Proton and bromine cleavage rank among the most extensively studied electrophilic substitution processes.[5–8] Substantial kinetic and stereochemical evidence has led to the proposal that such reactions occur by a concerted, front-side attack which proceeds through a transition state that involves a pentacoordinate carbon center.[5–9] A similar transition state has been suggested for a variety of elementary electrophilic processes (Figure 1).

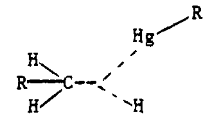

Figure 1. Idealized representation of the rate-limiting transition state proposed for the protonolysis of (n-alkyl)$_2$Hg by HA.

Table I. Deuterium Secondary Isotope Effect for Several Electrophilic Reactions[a]

substrate	electrophile	solvent	temp, °C	k_{CH_2}/k_{CD_2}[b]
$(C_7H_{15}CL_2)_2Hg$	HCl	dioxane	25	1.191 ± 0.005[e]
	Br_2	CCl_4[c]	0	1.257 ± 0.007
	Br_2	CH_3OH	20	1.223 ± 0.004
$(C_6H_{13}CL_2CH_2)_2Hg$	HCl	dioxane	25	1.008 ± 0.005
$(C_7H_{15}CL_2)Sn$-$[CH_2C(CH_3)_3]_3$	Br_2	CCl_4[c]	0	1.154 ± 0.007
	Br_2	CH_3OH CH_2Cl_2 (3:1)[d]	20	1.186 ± 0.004

[a] Initial composition: [substrate] = 0.1 M; [electrophile] = 0.01 M. A constant temperature (±0.02 °C) was maintained during the course of all cleavage reactions. The stereoselectivity of electrophilic cleavages has been found to vary substantially with reaction conditions.[5,7] Except where noted, the conditions employed in this study, insofar as possible, duplicate those under which the equivalent reaction employing a chiral substrate is reported to occur with maximum retention of configuration.[5,7] [b] The isotope effect associated with the competitive protic cleavage of **1**-d_0 and **1**-*1,1*-d_2 is given by k_{CH_2}/k_{CD_2} = ([octane-d_2]/[octane-d_0])$_{sc}$([octane-d_0]/[octane-d_2]). The corresponding expression for bromine cleavage is k_{CH_2}/k_{CD_2} = ([bromooctane-d_0]/[bromooctane-d_2])$_{sc}$([bromooctane-d_0]/[bromooctane-d_2]). The subscript sc refers to values obtained from a mixture identical in composition to that of the starting mixture. These ratios were determined by high-precision, whole-molecule mass spectrometry by simultaneously monitoring (for a total of 10000 scans) the M and M + 2 ions of the octane-d_0 and -d_2 and bromooctane-d_0 and -d_2 mixtures isolated at the completion of each reaction. Since neither octane nor bromooctane exhibit a significant (i.e., >1%) M − 2 ion, a correction for this factor was unnecessary. An ionizing voltage of 70 eV and a constant source pressure of 8.0 × 10^{-7} torr were employed. [c] Isamyl nitrite (0.01 M) added as a free-radical inhibitor.[7] [d] Reaction mixture was 0.1 M in (n-C_4H_9)$_4$NBr. [e] Indicated error is ±σ.

The secondary deuterium kinetic isotope effect associated with the competitive protonolysis of (di-n-octyl-*1,1*-d_0)mercury---(di-n-octyl-*1,1*-d_2)mercury, (**1**-d_0 and **1**-*1,1*-d_2, respectively) and (di-n-octyl-*2,2*-d_0)mercury---(di-n-octyl-*2,2*-d_2)mercury (**1**-d_0 and **1**-*2,2*-d_2, respectively) by anhydrous hydrogen chloride in dioxane is presented in Table I. Also listed are the corresponding data

$$[CH_3(CH_2)_6CH_2]_2Hg + [CH_3(CH_2)_6CD_2]_2Hg \xrightarrow[\text{dioxane}]{\text{HCl}} CH_3(CH_2)_6CH_3 + CH_3(CH_2)_6CD_2H$$

from the competitive bromine cleavage of **1**-d_0 and **1**-*1,1*-d_2, together with the equivalent data for trineopentyl(n-octyl-*1,1*-d_0)tin (**2**-d_0) and trineopentyl(n-octyl-*1,1*-d_2)tin (**2**-d_2). These data reveal (i) that a normal α-deuterium KIE prevails, i.e., $k_H/k_D > 1$, corresponding in this instance to ca. 1.10 per deuterium at 25 °C, (ii) that neither solvent nor the size or polarizability of the entering or leaving groups appear to have any significant influence on the magnitude of this effect, and (iii) that the corresponding β-deuterium isotope effect is negligible.

α-Deuterium secondary isotope effects arise in major part from the difference between the bending force constants at the isotopic center in the ground-state reactant and in the transition state.[2–4] This effect will the inverse ($k_D > k_H$) if the force constants are

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[1] (a) Supported by the NSF, Grant CHE 83-12730-01. (b) Jilin University, Changchun, Peoples' Republic of China.

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