and Y-I are stereoisomers with the phenolic hydroxyl groups hydrogen bonded primarily in one case to the carbonyl functional groups and in the other to the chlorine atoms. Two techniques are employed which have potentially general application. The isotope effect on the ester carbonyl stretching frequency produced by substitution of deuterium for hydrogen atoms of the phenolic hydroxyl groups provides a probe for the detection of hydrogen bonding to the carbonyl group, and the shift in the position of the ^{35}Cl nuclear quadrupole resonance[5] serves as a probe for hydrogen bonding to the chlorine atom.

The ir spectrum of solid Y-I in a Fluorolube mull shows a single sharp absorption at 1666 cm^{-1} with no other absorption between 1500 and 1800 cm^{-1} and with the OH stretching absorption in a broad region centered at about 3100 cm^{-1}. This is clearly inconsistent with structure B but in agreement with a hydroxy ester structure. Weltner has shown[6] that, in the vapor state, while monomeric CH_3COOD has the same carbonyl stretching frequency as the undeuterated acid, the deuterated hydrogen-bonded cyclic dimer $(CH_3COOD)_2$ has a carbonyl stretching frequency lowered 12 cm^{-1} from that of the undeuterated dimer. If Y-I has an $-OH\cdots O{=}C$ functional group which is absent in W-I, then Y-I alone should show a carbonyl frequency shift when its hydroxyl protons are replaced by deuterons. Indeed, crystalline Y-I prepared by crystallization of I from D_2O–acetone-d_6 and estimated from the relative areas of the OH and C=O absorptions to be at least 70% deuterated showed its carbonyl absorption (Fluorolube mull) at 1650 cm^{-1}, a shift of 16 cm^{-1} from the position of the undeuterated Y-I, and OD absorption at 2275 cm^{-1}. W-I prepared[2] by heating Y-I below its melting point (140°) for 1 hr showed no shift of the carbonyl absorption at 1700 cm^{-1} from the position of the undeuterated ester. The OD stretching frequency of W-I occurred at 2410 cm^{-1}. These results provide further evidence against structure B.

The ^{35}Cl nuclear quadrupole resonance[7] of a mixture of approximately 70% Y-I and 30% W-I showed the resonance of Y-I at 36.650 MHz at 25°. W-I showed resonances at 35.290 and 35.360 MHz. The separation of only 0.07 MHz between the latter two frequencies is probably due to packing of the molecules in two sets of nonequivalent positions with slightly different environments in the vicinity of the chlorine nucleus.[8] The separation of 1.3 MHz between the resonances of Y-I and W-I is much larger than would be expected for nonspecific crystal effects[8] and is in the direction expected.[9]

Our results establish that the yellow and white crystalline substances Y-I and W-I are not keto–enol tautomers as proposed by Hantzsch[2] but that Y-I has strong hydrogen bonds to the (identically situated) carbonyl oxygen atoms and W-I has strong hydrogen bonding to the (slightly nonequivalent) chlorine atoms. Intramolecularly hydrogen-bonded structures, C and D, are attractive possibilities,[2,10] and spectral evidence to be presented elsewhere together with molecular weight determinations shows that C and D are primary species present in dilute carbon tetrachloride or chloroform solution. However, intermolecular hydrogen bonding cannot be excluded in the structures of Y-I and W-I in the crystalline state.[11,12]

The crystal structures and the nature of the conversion of Y-I to W-I in the solid state are of continuing interest. The rearrangement proceeds at a reasonable rate at 125°, some 60° below the melting point of W-I. Differential thermal analysis shows a small endotherm at 130° corresponding to an enthalpy change of less than 1 kcal/mol.

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[5] C. T. O'Konski in "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1961.

[6] W. Weltner, *J. Am. Chem. Soc.*, **77**, 3941 (1955).

[7] We are indebted to Professor T. L. Brown and Mr. R. Tibbetts for the use of a Wilks Model NQR-1A instrument and for assistance with these measurements.

[8] P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **27**, 551 (1957).

[9] D. N. Kravtsov, A. N. Zhukov, B. A. Faingor, El. M. Rokhlina, G. K. Semin, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1703 (1968).

[10] See, for example, L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 490–496.

[11] For an example of a substance with intramolecular hydrogen bonds in dilute solution but chains of intermolecularly hydrogen-bonded molecules in the crystal, see G. W. R. Bartindale, M. M. Crowder, and K. A. Morley, *Acta Cryst.*, **12**, 111 (1959).

[12] See W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968.

[13] Sinclair Oil Co. Fellow, 1967–1968; National Science Foundation Fellow, 1968–1969.

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Minimization of Rearrangement Reactions in Mass Spectra by Use of Collisional Activation[1]

Sir:

Rearrangement and other unimolecular ionic reactions which exhibit low frequency factors, such as reaction A, Figure 1, must have lower activation energies to compete effectively with simple cleavage reactions of higher frequency factors, such as reaction B. Decompositions before the ions leave the source region shift the original distribution of precursor ion energies (curve I) to lower values (curve II); thus for ions decomposing in the metastable drift region (rates 10^5–10^6 sec^{-1}) rearrangement reactions such as A are strongly favored.[2] Conversely, it should be possible to minimize path A if the precursor ions can be formed with higher energies, such as curve III. Such energy values may result from collisions of the ions with neutral molecules in the metastable drift region. This is postulated to explain the fact that the relative rates of collision-induced metastable decompositions apparently are nearly independent of the original internal energy values of the ions of the precursor, in contrast to unimolecular decompositions occurring in either the ion source or the metastable drift region;[3] A and B are more nearly parallel for ions of energy distribution III than either I or II. Thus this reasoning would predict that rearrangement pathways should be less favored in collision-induced decompositions than in either the normal

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[1] Metastable Ion Characteristics. X. Paper IX: W. F. Haddon and F. W. McLafferty, *Anal. Chem.*, **41**, 31 (1969).

[2] F. W. McLafferty and R. B. Fairweather, *J. Am. Chem. Soc.*, **90**, 5915 (1968).

[3] W. F. Haddon and F. W. McLafferty, *ibid.*, **90**, 4745 (1968).

Table I. Collision-Induced Metastable Decompositions of $C_2H_5O^+$ Ions

Compound	Type[a]	$C_2H_3O^+$[b]	CHO^+	$C_2H_3^+$	H_3O^+	CH_3^+
$CH_3CH(CH_3)OHOH$	I	1.0[c]	1.1	0.6_2	0.38	0.24
$C_2H_5CH(CH_3)OH$	I	*d*	1.0	0.5_9	0.3_5	0.18
$CH_3COCH(CH_3)OH$	I	0.9	1.1	0.7_5	0.4_3	0.2_8
$(CH_3)_2CHOCH(CH_3)_2$	I	0.37	0.9	0.4_3	0.21	0.23
$HCOOC_2H_5$	I, II[f]	0.9[e]	1.0	0.7_3	0.4_8	0.6[e]
$C_2H_5OC_2H_5$	I or II[g]	$1._3$	1.1	0.6_5	0.4_3	0.3_0
$C_2H_3OC_2H_5$	I or II	1.0[e]	*d*	*d*	0.5[e]	*d*
$HOCH(CH_3)CH_2CH_2OH$	I, III	1.0[e]	1.3	0.9	0.7	*d*
$C_2H_5OCH_2CH_2OH$	II, III	2[e]	1.2	0.7	0.7	*d*
$CH_3CH_2CH_2OH$	III	*d*	*d*	*d*	$1._2$	*d*
$C_2H_5CH_2CH_2OH$	III	*d*	*d*	*d*	$1._2$	*d*
$HOCH_2CH_2CH_2OH$	III	*d*	*d*	*d*	1.2	*d*
$CH_3OCH(CH_3)CH_2CH_2OH$	III	*d*	*d*	*d*	0.9	*d*
$HOCH_2CH_2OCH_3$	III, IV	<0.1	2.0	<0.1	0.1_5	0.2_8
$CH_3OCH_2CH_2OCH_3$	IV	<0.1	2.0	<0.1	<0.02	0.1_8
$NCCH_2CH_2OCH_3$	IV	*h*	2.0	<0.1	<0.02	*h*

[a] Expected structure of $C_2H_5O^+$ ion: I, $CH_3CH{=}OH^+$; II, $CH_3CH_2O^+$; III, $HOCH_2CH_2^+$; IV, $CH_3O{=}CH_2^+$. [b] Product ion of the metastable decomposition producing the peak measured. [c] Per cent abundance of the collision-induced metastable peak relative to the abundance of the $C_2H_5O^+$ peak measured as described in ref 1 and 3; drift region pressure *ca.* 5×10^{-6} Torr. [d] Not measurable due to interference by peak from neutral fragments and/or low $C_2H_5O^+$ abundance. [e] Error *ca.* ±50%. [f] 35–43% II.[11] [g] Reference 11. [h] Value not measured.

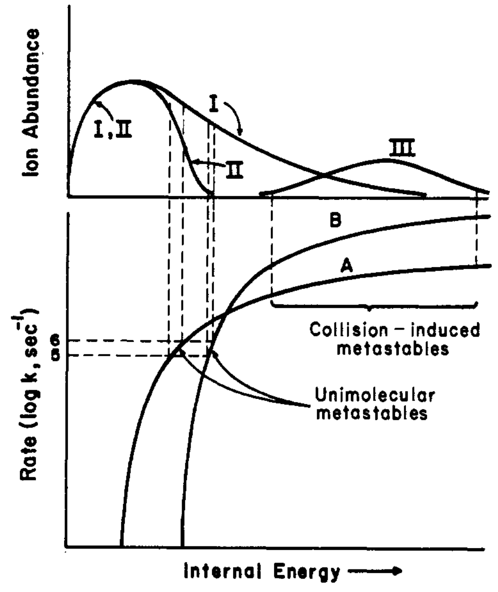

Figure 1. Lower curves: relation of the internal energy of the precursor ions to the corresponding rates of the hypothetical unimolecular reactions A and B. Upper curves: hypothetical abundance of the precursor ions with a particular energy content *vs.* energy: I, ions as initially formed in the source region; II, ions which reach the metastable drift region without decomposition; III, ions after collision in the metastable drift region (omitting higher energy precursors which yield product ions too unstable to be recorded).

or metastable mass spectra. Data on toluene and $C_2H_5O^+$ decompositions presented below support these conclusions.

The abundances of $(M - H)^+$ and $(M - D)^+$ in the spectra of $C_6H_5CD_3$ and $C_6D_5CH_3$ indicate that the processes which lead to scrambling of the positions of the hydrogen atoms have much faster rates than the processes which lead to specific loss of any hydrogen atom which was originally in the α position;[4,5] Meyer and Harrison[6] calculate a 20:1 ratio for the rates of scrambling *vs.* H loss for a particular mechanistic scheme. We find that collision-induced metastables from $C_6H_5CD_3$ show only 60 ± 5%[7] of the isotope scrambling determined for unimolecular metastables.[8] This indicates that the rate ratio for scrambling *vs.* H loss is reduced to approximately 4:1 on the same basis[6] assuming no change in the isotope effect.

Unimolecular metastable ion characteristics of $C_2H_5O^+$ ions from $HOCH_2CH_2R$, $HOCH(CH_3)R$, and CH_3CH_2OR compounds appear to be identical,[10] supporting evidence[11] for isomerization of the initial $C_2H_5O^+$ ions to a protonated oxirane structure prior to or during fragmentation. Recently Harrison and Keyes reported studies of 2-propanol-2-^{13}C;[12] ^{13}C retention in CHO^+ indicates that only 64% (using 20-eV electrons) or 52% (using 70-eV electrons) of the $C_2H_5O^+$ ions are isomerized in these higher energy decompositions. Isomerization is reduced even further in the collision-induced decompositions reported in Table I. For $C_2H_5O^+$ ions with energy

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(4) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, Chapter 10.

(5) J. G. Burr and R. A. Meyer, *J. Chem. Phys.*, **40**, 2046 (1964).

(6) F. Meyer and A. G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).

(7) Standard deviation of values determined from abundances of *m/e* 95 → 94 and 95 → 93 measured at six different pressures of admitted air using the techniques described previously.[1,3]

(8) Jennings[9] also investigated $C_6H_5CD_3$. He reported no data for the M − H reaction, but found a similar extent of H–D randomization in the unimolecular and collision-induced processes forming lower mass ions.

(9) K. R. Jennings, *J. Mass. Spectrom. Ion Physics*, **1**, 277 (1968).

(10) T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 5021 (1966); F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967).

(11) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 2054, 3118 (1963); A. G. Harrison, A. Ivko, and D. Van Raalte, *ibid.*, **44**, 1625 (1966).

(12) A. G. Harrison and B. G. Keyes, *J. Am. Chem. Soc.*, **90**, 5046 (1968).

insufficient to decompose before reaching the collector, a major portion of those formed from the 2-alkanols must have a different structure (presumably $CH_3CH{=}OH^+$) from those originating from 1-alkanols. Metastables corresponding to $C_2H_5O^+ \rightarrow H_3O^+$ are approximately 35% as abundant for 2-alkanols as for 1-alkanols, representing the maximum proportion of the $C_2H_5O^+$ ions that can have a common structure.[13] Also for 2-alkanols the collision-induced metastables for $C_2H_5O^+ \rightarrow CHO^+$ are not flat topped, as observed for the unimolecular metastables,[10] indicating that a different transition state is involved. The $C_2H_5O^+$ ion from isopropyl ether should also have the structure $CH_3CH{=}OH^+$;[14] its characteristics are consistent with less isomerization than for the $C_2H_5O^+$ of the 2-alkanols.[13]

The metastable characteristics of the $C_2H_5O^+$ ions from the ethoxy compounds are identical within experimental error to those of the 2-alkanols. However, pathways for direct formation of $CH_3CH{=}OH^+$ as well as $CH_3CH_2O^+$ are indicated,[11] so the extent of the isomerization $CH_3CH_2O^+ \rightarrow CH_3CH{=}OH^+$ before metastable decomposition is not clear. $C_2H_5O^+$ ions from CH_3OCH_2R compounds appear to represent a separate structure, consistent with our previous findings.[10]

Note that the collision-induced process will provide a lower probability for a rearrangement reaction only if a competitive pathway of higher frequency factor is operative; thus collision-induced spectra could resemble normal spectra, as found by Jennings.[9] The reduction or elimination of rearrangement processes in mass spectra has obvious important applications for structural studies;[2] for example, the data cited indicate improved usefulness for isotopic studies of aromatic compounds and for distinguishing $HOCH_2CH_2$– and $HOCH(CH_3)$– moieties in molecular structures.[15]

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(13) Note that lowering the energy of the $C_2H_5O^+$ ions should lower the rate of isomerization before collision but should have little effect on the rate of collision-induced isomerization.

(14) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

(15) The financial support of the National Institutes of Health is gratefully acknowledged (Grants GM 12755 and FR 00354).

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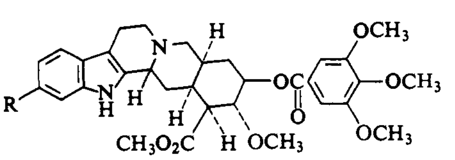
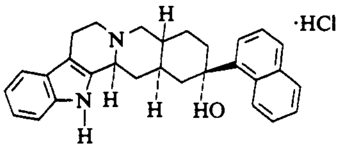
Induction of Fluorescence Polarization in Intramolecular Electronic Energy Transfer

Sir:

In a recent paper we reported[1] observation of 100% intramolecular singlet–singlet electronic energy transfer between the nonconjugated chromophores of the indole alkaloids reserpine (I), deserpidine (II), 17-naphthylyohimbol (III), and rescinnamine. A combination of exchange and resonance mechanisms was postulated to explain this high efficiency. The average donor–acceptor separation (6–12 Å) was too great in all four cases to rationalize the transfer of all singlet excitation *via* the Förster mechanism, yet small enough to allow the possibility of physical overlap of donor and acceptor π orbital systems.



I, R = OCH_3
II, R = H



III

For the purpose of elucidating further the mechanism of this energy transfer as well as determining the presence of any preferred transition dipole–dipole orientations of donor and acceptor, we have studied the polarization of reserpine and 17-α-naphthylyohimbol fluorescence[2] as a function of solvent viscosity and exciting wavelength.[3,4] Solutions were invariably 6.7×10^{-4} *M* in each of five solvents:[5] propylene glycol, isopropyl alcohol, ethanol, methanol, and anhydrous ether. Measurements of the degree of polarization were obtained at the fluorescence maximum with excitation at 300 and 280 nm. A measurement at 77°K in ethanol glass was also recorded. The degree of polarization (*P*) was calculated from eq 1 where $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities at mutually

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \tag{1}$$

parallel and perpendicular settings of Glan–Thompson prisms mounted at 45° angles to both excitation source and detector.[6]

Two factors should affect the polarization of the fluorescence of the acceptor moiety in the alkaloids studied. First is the rotational depolarization, the degree varying inversely with solvent viscosity. Movements of the acceptor moiety about flexible bonds would be expected to contribute more to this form of depolarization than rotation of the entire molecule, due to the large molecular volume of the alkaloids. Rotational depolarization may be eliminated by observing the polarization of emission of the compound at 77°K in a rigid glass.

The second factor is depolarization due to the energy-transfer process itself. Transfer due to a long-range

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(1) R. D. Rauh, T. R. Evans, and P. A. Leermakers, *J. Am. Chem. Soc.*, **90**, 6897 (1968).

(2) Rescinnamine does not emit at room temperature, and hence is necessarily omitted from this study.

(3) P. P. Feofilov, "The Physical Basis of Polarized Emission," Consultants Bureau, New York, N. Y., 1961, pp 108–171.

(4) G. Weber, *Trans. Faraday Soc.*, **50**, 552 (1954).

(5) The trivial mechanism of energy transfer does not occur at this concentration; see ref 1.

(6) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 3037 (1965).