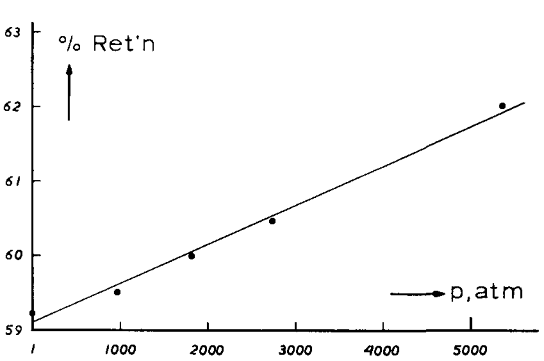
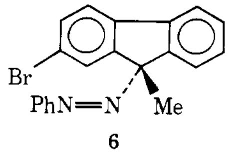


Figure 1. The effect of pressure on the stereochemistry of deamination of **5**.

ensure complete reaction, and parallel experiments were carried out in the same glassware at atmospheric pressure. On the basis of the evidence just quoted it is reasonable to assume that the lifetime of the loose pair should increase under pressure and that the rates of tight ion-pair formation and of collapse of the latter to covalent product should be retarded. Thus at face value the equilibration of the enantiomeric loose pairs should correspondingly be promoted by the application of pressure.

However, this is not the case, as is indicated by the data in Figure 1; retention is clearly favored under pressure. It can be readily shown from a steady-state treatment that $V_c^{\ddagger} - V_e^{\ddagger} = RT\,\partial \ln (100/r - 1)/\partial p$, where e and c denote equilibration and collapse of the loose pair and where r is the percent retention. When the appropriate plot is made, it is found that the transition state for inversion is 0.55 cm^3/mol *more* voluminous than that for retention. On the basis of the literature quoted above,[8-14] a large volume increase must occur when the loose pair becomes tight. This increase will be especially large in a solvent as methylene chloride: at least 10 cm^3/mol, and possibly much more.[10] The measurements reported here therefore indicate that inversion also has a large positive activation volume (larger than that of retention by 0.55 cm^3/mol).

Our interpretation of this fact is that the loose pair racemization is inhibited by viscosity increases. Pressure is known[18] to cause drastic increases in the viscosity of liquids; accordingly, diffusion controlled reactions are retarded regardless what volume changes characterize the rapid steps. Related pressure effects have been described by Neuman, who has found pressure induced increases in the ratio of cage to escape products in radical reactions;[19a] furthermore, changes were also observed in the distribution of cage products, such as recombination and disproportionation products.[19] These changes were ascribed to pressure induced viscosity changes, and their effect on rotational motions of the radicals in the cage. Independent indications that this is so are provided by work of Johnson and Seltzer,[20] who have found that the mere use of more viscous media led to increased retention in the decomposition of resolved azo compound **6**, and by results of Bartlett and McBride,[21] showing that complete retention can be ensured in the photodecomposition of **7** by the use of a solid, low temperature matrix.



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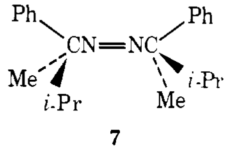

7

In a similar experiment, we allowed the decomposition of **5** to occur in the solid phase (crystals) at room temperature. The product was purified, and subsequently observed to have (65.8 ± 0.10%) retained and (34.2 ± 0.10%) inverted configuration. If this point is assumed to lie on the same straight line as the high pressure results, the corresponding pressure would be about 13 000 atm. Most organic solids show a volume decrease of 5–15% on fusion, and most liquids have a compression of about 25% at 13 000 atm; it is interesting that the result in the solid phase is indeed similar to that in highly compressed methylene chloride.[22]

We may summarize our observations with the statement that they comprise the first evidence for viscosity effects on the behavior of ion pairs.

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References and Notes

(1) E. H. White, *J. Am. Chem. Soc.*, **76**, 4497 (1954); 77, 6008, 6011 (1955).
(2) E. H. White, R. H. McGirk, C. A. Aufdermarsh, H. P. Tiwari, and M. J. Todd, *J. Am. Chem. Soc.*, **95**, 8107 (1973).
(3) E. H. White and J. Stuber, *J. Am. Chem. Soc.*, **85**, 2168 (1963).
(4) E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).
(5) E. H. White and C. A. Aufdermarsh, *J. Am. Chem. Soc.*, **80**, 2597 (1958); **83**, 1179 (1961).
(6) E. H. White and C. A. Elliger, *J. Am. Chem. Soc.*, **89**, 165 (1967).
(7) Phenyl *p*-chlorophenyldiazomethane formation contributes to the racemization, but only to a minor degree. Decomposition of **5** in the presence of 36 molar equiv of diazomethane led to the formation of a maximum of 0.5% of the diazo species (from absorption intensity at 526 nm); 58.5% retention of configuration occurred in this run. Further, decomposition of **5** in the presence of 3 molar equiv of *O*-deuterionaphthoic acid (> 95% O-D by NMR) led to ester containing no detectable deuterium (< 0.01 atom per molecule).
(8) K. R. Brower, *J. Am. Chem. Soc.*, **94**, 5747 (1972).
(9) W. J. le Noble, B. L. Yates, and A. W. Scaplehorn, *J. Am. Chem. Soc.*, **89**, 3751 (1967).
(10) W. J. le Noble and A. R. Das, *J. Phys. Chem.*, **74**, 3429 (1970); S. Claesson, B. Lundgren, and M. Szwarc, *Trans. Faraday Soc.*, **66**, 3053 (1970); B. Lundgren, S. Claesson, and M. Szwarc, *Chem. Scr.*, **5**, 60 (1974).
(11) W. J. le Noble and S. K. Palit, *Tetrahedron Lett.*, 493 (1972).
(12) S. D. Hamann, *Mod. Aspects Electrochem.*, **9**, 47 (1974).
(13) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967).
(14) Apparent exceptions include the pressure-promoted bleaching of Malachite Green by base[15] (however, see also ref 16), and the pressure retarded photoionization of nitrophenol[17] (it seems probably that this reaction is not really exceptional if the probable charge distribution in the excited states is considered).
(15) D. T. Y. Chen and K. J. Laidler, *Can. J. Chem.*, **37**, 599 (1959).
(16) C. D. Ritchie, D. J. Wright, D. S. Huang, and A. A. Kamego, *J. Am. Chem. Soc.*, **97**, 1163 (1975).
(17) S. D. Hamann, *J. Phys. Chem.*, **70**, 2418 (1966).
(18) P. W. Bridgman, "The Physics of High Pressure", Bell, London 1952.
(19) (a) R. C. Neuman, Jr., *Acc. Chem. Res.*, **5**, 381 (1972); (b) V. M. Zhulin and M. G. Gonikberg, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (*English transl.*), 284 (1972).
(20) R. A. Johnson and S. Seltzer, *J. Am. Chem. Soc.*, **95**, 938 (1973). The authors ruled out more trivial explanations such as a simple viscosity induced decrease in escape from the cage.
(21) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).
(22) As a referee has pointed out, it is possible that crystal dislocations rather than internal pressures are responsible for these effects.

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The Intramolecular Hydrogen Bond in Malonaldehyde[1]

Sir:

Recently two quantum mechanical calculations have been published[2] dealing with the structure of the internally hydrogen-bonded form of malonaldehyde (Figure 1). We have partially analyzed the microwave spectra of a number

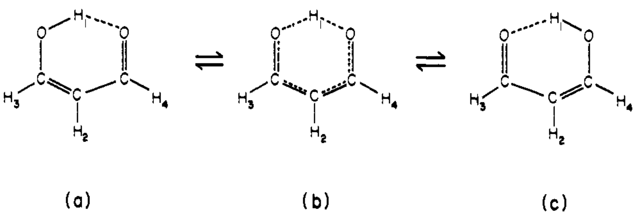

Figure 1. Hydrogen-bonded, tunneling structure of malonaldehyde, CHCHOHOCH.

Table I. Rotational Constants, Centrifugal Distortion Coefficients, Moments of Inertia, and Inertial Defects of ^{16}O-^{16}O Malonaldehyde[a]

Vibrational state	Ground state	Lowest excited state
A	9833.855 ± 0.001	9846.055 ± 0.001
B	5212.538 ± 0.002	5158.734 ± 0.001
C	3404.363 ± 0.001	3383.234 ± 0.001
Δ_J	0.003 86 ± 0.000 03	0.003 06 ± 0.000 02
Δ_{JK}	−0.000 25 ± 0.000 03	−0.011 00 ± 0.000 03
Δ_K	0.001 19 ± 0.000 08	0.012 42 ± 0.000 07
δ_J	0.001 43 ± 0.000 01	0.001 09 ± 0.000 01
δ_K	0.007 71 ± 0.000 04	0.000 44 ± 0.000 05
I_a	51.3918	51.3281
I_b	96.9545	97.9657
I_c	148.4504	149.3775
$I_c - I_a - I_b$	0.1041	0.0837

[a] The rotational constants and centrifugal distortion coefficients are in MHz, while the moments of inertia and inertial defects are in amu Å^2. Errors are from least-squares fit. Actual errors may be several times larger.

of isotopic species of malonaldehyde, obtaining results which can be compared with those predicted.

In the symmetrically hydrogen-bonded form shown in Figure 1b or in the average of Figure 1a and 1c, H_3 and H_4 are equivalent. The Pauli exclusion principle then requires that the rotational energy levels have nuclear spin degeneracies of three or one, depending on the values of the oblate and prolate quantum numbers of these rotational levels. Rotational transitions between levels with spin degeneracies of three will be three times as intense as those between levels with a spin degeneracy of one. Transitions between rotational levels of different spin degeneracy are, of course, forbidden. The rotational transitions of the ground vibrational state of the normal isotopic species of malonaldehyde show alternating intensities of approximately three to one, proving that the appropriate average structure has a twofold axis of symmetry. The rotational constants, moments of inertia, and other relevant spectral parameters of this state are shown in Table I. The small positive inertial defect [$I_c - I_a - I_b$] is strong evidence for an essentially planar structure.

A second set of rotational transitions, almost as strong as the ground state but with opposite nuclear spin weights, was also observed. Relative intensity measurements place this vibrational level 16 ± 14 cm^{-1} above the ground state, while its positive inertial defect, as indicated in Table I, suggests that it is due to an excited in-plane vibrational state.[3]

These results would seem to rule out: (a) a symmetrical (resonating) structure with a single potential minimum for H_1, because it would not have such a low-lying second vibrational level; (b) a double minimum potential with a high barrier between the two minima, because this would cause the two lowest vibrational states to coalesce, thus eliminating the observed three-to-one ratio of nuclear spin weights.

Table II. Rotational Constants, Moments of Inertia, and Inertial Defects of ^{18}O-Substituted Malonaldehyde[a]

	^{18}O-^{16}O Malonaldehyde ground state	^{18}O-^{18}O Malonaldehyde ground state
A	9590.59 ± 0.01	9340.02 ± 0.02
B	5042.13 ± 0.01	4883.68 ± 0.02
C	3302.46 ± 0.01	3204.70 ± 0.02
I_a	52.6953	54.1090
I_b	100.2313	103.4833
I_c	153.0311	157.6993
$I_c - I_a - I_b$	0.1045	0.1070

[a] The rotational constants are in MHz, while the moments of inertia and inertial defects are in amu Å^2.

Table III. O···O Distances in Malonaldehyde

			O···O distance (Å)
A.	Determined by ^{18}O substitution		
	^{18}O-^{16}O malonaldehyde		2.55[a]
	^{18}O-^{18}O malonaldehyde		2.55
		Av	2.55
B.	Calculated		
	Karlstrom et al.[2a]	ab initio	2.63 (C_s)
		CNDO/2	2.38 (C_s)
	Isaacson and Morokuma[2b]	ab initio	2.28 (C_{2v})

[a] If the instrumental resolution had been sufficiently lower than it actually was, the corresponding transitions from the two low-lying states would have coalesced, the alternating intensities would have been lost, and the accuracy of frequency measurement degraded because of the breadth of the coalesced line pairs. The molecule would then have been treated as essentially nontunneling, i.e., locked in one minimum. This line breadth would produce an uncertainty of about 0.1 Å for the O-O distance obtained by the Costain-Kraitchman[5,6] method. We believe this is an upper bound for the actual error.

We thus believe the molecule has a symmetrical double minimum potential surface with a relatively low barrier between the two minima so that rapid tunneling occurs between the two asymmetric forms of malonaldehyde.

Additional information was obtained from the spectra of the ^{18}O-^{16}O and ^{18}O-^{18}O species.[4] The ground state moments of inertia of these species (Table II), combined with those of the ^{16}O-^{16}O form in the usual way,[5-7] give the O-O distance listed in Table III.

Recent theoretical calculations can be compared with our results. Karlström et al.[2a,8] obtain a double minimum potential with a barrier low enough so that it may be compatible with the observed tunneling. Their O···O distance is slightly longer than our rough value. On the other hand, Isaacson and Morokuma[2b] arrive at a single minimum potential and much too short an O···O distance, but feel their results are not conclusive.

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References and Notes

(1) This research was supported in part by a grant extended Harvard University by the National Science Foundation, MPS 73 08486.

(2) G. Karlstrom, H. Wennerstrom, B. Jonsson, S. Forsen, J. Almhof, and B. Roos, *J. Am. Chem. Soc.*, **97**, 4188 (1975); (b) A. D. Isaacson and K. Morokuma, *ibid.*, **97**, 4453 (1975).

(3) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **40**, 3142 (1964).

(4) ^{18}O enriched malonaldehyde was obtained by acid hydrolysis of malonaldehyde bis(dimethyl acetal) in ^{18}O enriched water, followed by gas chromatographic purification at 85 °C on a 2 ft copper column packed with

Porapak Q.
(5) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).
(6) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).
(7) C. W. Gillies, Ph.D. Thesis, University of Michigan, 1972.
(8) G. Karlstrom, B. Jonsson, B. Roos, and H. Wennerstrom, preprint, have recently added configuration interaction, lowering the barrier somewhat.
(9) Assistance from the National Science Foundation under the Small College Faculty Program is gratefully acknowledged.

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Kinetics of Reduction of Horse-Heart Ferricytochrome c by Catechol

Sir:

Ferricytochrome *c* (cyt *c*(III)) has been the subject of numerous studies employing a broad spectrum of reductants which have been selected to probe the mechanism of electron transfer to the ferriprotein. Rate and activation parameters have been determined for the reduction of cyt *c*(III) by relatively simple reductants such as Cr_{aq}^{2+}, $Ru(NH_3)_6^{2+}$, e_{aq}^-, $Fe(EDTA)^{2-}$, ascorbate, superoxide anion, and dithionite.[1] On the other extreme, studies of electron transfer to cyt *c*(III) in enzymatic systems[2] and even from cyt *c*(II)[3] have been undertaken. There is, however, a paucity of information pertaining to the mechanism of reduction of cyt *c*(III) by mild, multielectron reductants such as catechol (1,2-dihydroxybenzene) and catechol derivatives (e.g., 3,4-dihydroxyphenylalanine and epinephrine).[4] Although such studies may not have direct biological significance,[5] they should shed light on the mechanism of electron transfer in cytochrome systems.

This report summarizes the results of a series of experiments designed to examine possible pathways for electron transfer from catechol to ferricytochrome *c*. The rate expression for electron transfer contains terms which are first and second power in [HC⁻] and [cyt *c*(III)], respectively, rate = $d[\text{cyt } c(\text{II})]/dt = k[\text{cyt } c(\text{III})]^2[\text{HC}^-]$, where HC⁻ represents catechol anion and $k = (4.51 \pm 0.12) \times 10^7\ M^{-2}\ s^{-1}$.

All experiments were conducted under nitrogen at 25.0 °C, $\mu = 0.10$(NaCl) and pH ranging from 7.53 to 6.02 (phosphate buffer).[6] Concentration of catechol was at least 200-fold mole excess in all runs. Kinetics data were obtained by recording absorbance vs. time for the appearance of the 550-nm band of cyt *c*(II). A few experiments were conducted by attempting to monitor absorbance changes at 556.5, 542, and 526.5 nm, isosbestic points in the cyt *c*(II)-cyt *c*(III) spectra. No change in optical density was observed at any of these wavelengths during the course of reduction, suggesting that any intermediates on the reaction pathway exist in low concentrations.

The results of the kinetics experiments appear in Table I. In spite of the large excess [catechol], linear plots of $-\ln (A_\infty - A_t)$ vs. time[7] were never obtained. Rather, plots of $1/(A_\infty - A_t)$ vs. time were always linear (for at least 85% reaction, Figure 1), implying a rate law with a second-order dependence on [cyt *c*(III)], the reactant in limiting concentration,

$$\text{rate} = d[\text{cyt } c(\text{II})]/dt = k_{\text{obsd}}[\text{cyt } c(\text{III})]^2$$

where k_{obsd}[8] is some function of [catechol] and [H⁺], and k_{obsd} is a pseudo-second-order rate constant. Plots of k_{obsd} vs. [catechol] at each selected pH were linear, however, demonstrating the first-order dependence of the reaction rate on [reductant]. Indeed, constant values of $k' = k_{\text{obsd}}/[\text{catechol}]$ were obtained at each pH and these values also appear in Table I.

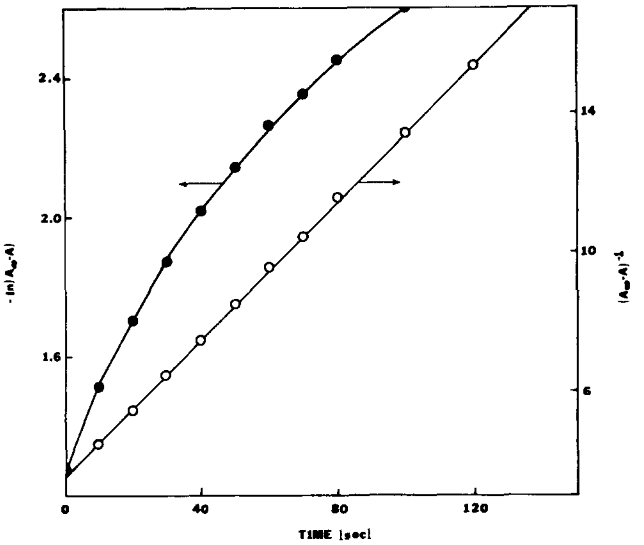

Figure 1. Plots of $-\ln (A_\infty - A)$ vs. time (filled circles) and $(A_\infty - A)^{-1}$ vs. time (open circles) for a representative run. [Catechol] = 1.53×10^{-2} M, [cyt *c*(III)] = 7.57×10^{-6} M, pH 7.01 (phosphate), μ = 0.10 (NaCl), λ 550 nm, and *T* = 25.0 °C.

Table I. Kinetics Data for the Reduction of Ferricytochrome *c* by Catechol (25.0 °C, μ = 0.10 (NaCl))

pH	10^2[catechol],[a,b] M	$10^{-3}\ k_{\text{obsd}}$,[c] $M^{-1}\ s^{-1}$	$10^{-5}\ k'$,[d] $M^{-2}\ s^{-1}$
7.53	0.589	5.11	8.67
7.53	1.14	10.0	8.77
7.53	2.19	19.4	8.86
7.53	4.02	34.7	8.63
		at pH 7.53 $\bar{k}'$ =	8.73 ± 0.10
7.01	0.411	0.992	2.41
7.01	0.806	1.79	2.22
7.01	0.999	2.21	2.21
7.01	1.91	4.26	2.24
7.01	2.89	7.36	2.55
7.01	3.49	8.73	2.50
		at pH 7.01 $\bar{k}'$ =	2.36 ± 0.15
6.54	1.04	0.747	0.718
6.54	1.49	1.05	0.705
6.54	1.90	1.36	0.716
6.54	3.55	2.56	0.721
		at pH 6.54 $\bar{k}'$ =	0.715 ± 0.007
6.01	2.32	0.670	0.289
6.01	5.47	1.62	0.296
6.01	7.39	2.09	0.283
6.01	10.0	3.08	0.307
		at pH 6.01 $\bar{k}'$ =	0.294 ± 0.010

[a] [catechol] represents total of all catechol species, HC⁻ and H_2C. [b] [cyt *c*(III)] = 1.80×10^{-5} M for pH 7.53 and 7.01, and 1.63×10^{-5} M for pH 6.54 and 6.02. [c] Each entry is the average of at least three runs. Values of k_{obsd} calculated as $k_{\text{obsd}} = sl(\Delta\epsilon)$, where *s* is the slope of a plot of $1/(A_\infty - A_t)$ vs. time, *l* is the pathlength (2 cm), and $\Delta\epsilon$ is the difference in molar extinction coefficients for cyt *c*(III) and cyt *c*(II) at 550 nm ($1.85 \times 10^4\ M^{-1}\ cm^{-1}$, E. Margoliash and N. Frohwirt, *Biochem. J.*, **71**, 570 (1959)). [d] *k'* is defined as $k' = k_{\text{obsd}}/[\text{catechol}]$.

The rate of cyt *c*(III) reduction was found to increase with increasing pH, and a linear plot of *k'* vs. 1/[H⁺] was obtained. Thus the rate law for electron transfer might be expressed as

$$\text{rate} = k[\text{cyt } c(\text{III})]^2[\text{catechol}][\text{H}^+]^{-1}$$