

Table VI. Rate Constants for Charge-Transfer Quenching of Triplet Phenyl Ketones

Diene	IP ^a	$k_{ct}, 10^7 M^{-1}$	
		Predicted	Obsd
Triethylamine	7.50	600	350 ^b
Dibutyl sulfide	8.30	50	60 ^{c,d}
sec-Butylamine	8.70	11	15 ^{c,e}
n-Butyl mercaptan	9.14	2.5	1.4 ^f
Benzene	9.25	1.8	$\leq 0.002^g$
Isoprene	8.84	7	
1,3-Pentadiene	8.68	13	
Cyclopentadiene	8.57	18	
2,4-Hexadiene	8.48	25	
1,3-Cyclohexadiene	8.40	32	
2,5-Dimethyl-2,4-hexadiene	7.91	150	

^a References 45 and *d* in Table V; also R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965. ^b P. J. Wagner and A. E. Kempainen, *J. Amer. Chem. Soc.*, **91**, 3085 (1969). ^c Benzophenone. ^d J. B. Gutenplan and S. G. Cohen, *J. Chem. Soc. D*, 247 (1969). ^e S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968). ^f P. J. Wagner and R. G. Zepp, *ibid.*, **93**, 4958 (1971). ^g Reference 29.

to deduce its quenching potential. In this regard, the behavior of conjugated dienes is both interesting, since their IP's are appreciably lower than those of monoolefins, and important, since dienes are widely used to monitor triplet yields and lifetimes. Since the original submission of this paper, two groups of workers^{50,51} have ascribed the previously reported diene quenching of alkanone fluorescence,⁵² which is accompanied by

(50) N. C. Yang, M. H. Hui, and S. A. Bellard, *ibid.*, **93**, 4056 (1971).

(51) R. R. Hautala and N. J. Turro, *ibid.*, **93**, 5595 (1971).

(52) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).

cycloadduct formation,^{50,53} to charge-transfer quenching of n, π^* singlets. Interestingly, one line correlates the singlet quenching rates of both dienes and monoolefins as a function of quencher IP.⁵⁰ Moreover, actual k_q (singlet) values for monoolefins are very similar to the k_q (triplet) values we report here. Therefore, charge-transfer quenching of ketone triplets undoubtedly competes with electronic energy transfer for dienes with especially low IP's, as indicated by the predicted rate constants in Table VI for charge-transfer quenching by commonly used dienes. The very low quantum yield oxetane formation observed upon irradiation of benzophenone with 2,3-dimethyl-1,3-butadiene^{54,55} and other dienes⁵⁵ very likely involves such a process. Figure 3 would predict a rate constant for quenching of triplet ketones by 2,3-dimethyl-1,3-butadiene on the order of $10^8 M^{-1} \text{sec}^{-1}$, much larger than the $10^6 M^{-1} \text{sec}^{-1}$ value estimated.⁵⁵ However, that estimate must be low because it assumed no radiationless decay due to reversible complexation.

Finally, we can note that only $\sim 1\%$ CT quenching is expected to compete with triplet energy transfer to 1,3-pentadiene, so that triplet counting by that diene⁵⁶ should not be endangered.

Acknowledgment. Preliminary work was performed by Mr. John Barber and supported by Research Corporation. A National Science Foundation grant also provided assistance.

(53) J. A. Barltrop and H. A. J. Carless, *J. Chem. Soc. D*, 1637 (1970).

(54) J. Saltiel, R. M. Coates, and W. G. Dauben, *J. Amer. Chem. Soc.*, **88**, 2745 (1966).

(55) J. A. Barltrop and H. A. J. Carless, *ibid.*, **93**, 4794 (1971).

(56) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965)

Intermolecular Hydrogen Transfer Reactions in the Mass Spectra of Dialkyl Malonates

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Abstract: Intermolecular hydrogen transfer reactions of dialkyl malonates have been investigated under conditions of low-pressure mass spectrometry. Extensive deuterium labeling, which was exhaustive in the case of dimethyl, diethyl, di-*n*-propyl, and diisopropyl esters, aided in determining the sources of hydrogen transferred in the formation of $M + H$, and the identities of the most effective proton donors. It was concluded that the high reactivity which is characteristic of this class of compounds is due mainly to ions which bear labile hydrogens bound to oxygen, including $\text{ROC}(\text{OH})\text{CH}_2^+$, $\text{HOCOCH}_2\text{C}(\text{OH})_2^+$, and $\text{ROCOCH}_2\text{C}(\text{OH})_2^+$. No evidence was found for fragment ions formed by decomposition of the $M + H$ species.

Intermolecular hydrogen transfer reactions which lead to protonated molecular ions ($M + H$) are common processes in low-pressure organic mass spectrometry. Examples of their occurrence and recognition of their dependence upon pressure are available in the early literature, and include aliphatic ethers,¹ nitriles,^{2,3} amines, and other heteroatom-containing

molecules.¹ The utility of these ions in establishment of molecular weight was recognized by McLafferty,¹ but their mechanisms of formation in most cases have remained obscure in spite of the development of gaseous ion-molecule chemistry.⁴ Relatively few studies

(2) J. H. Beynon, G. R. Lester, R. A. Saunders, and A. E. Williams, *Trans. Faraday Soc.*, **57**, 1259 (1961).

(3) F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).

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

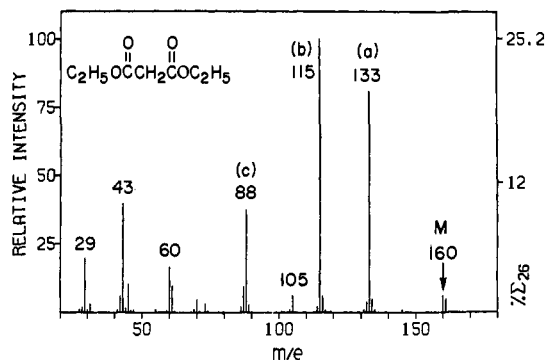
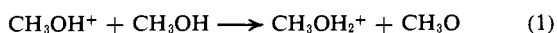
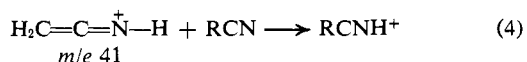


Figure 1. Mass spectrum of diethyl malonate (2a).

have been carried out to systematically determine the source of hydrogen which is transferred, and the relationships between ion structure and the characteristically large cross sections for these reactions. Formation of $M + H$ from methanol and ethanol and their deuterium labeled analogs was studied in detail by Futrell and coworkers using both conventional⁵ and tandem instruments.⁶ They found that in the case of methanol the major reactions involved proton transfer of oxygen-bound hydrogen from the three species shown in eq 1–3. Deuterium labeled nitriles were investigated by



Heerma and Dijkstra,⁷ who concluded that the favored route for $M + H$ formation was proton transfer⁸ of the hydrogen bound to nitrogen in the McLafferty rearrangement product, m/e 41³ (eq 4).



We have sought to further examine the sources of hydrogen transferred and the structures of ions involved in the formation of $M + H$ ions under the normal conditions of electron ionization mass spectrometry,⁹ in which the reactant ions can have a large amount of internal energy. Requirements for a suitable system included (1) the formation of $M + H$ peaks of reasonable intensity ($>1\%$ Σ) at relatively low pressures in a conventional instrument; (2) that a mass spectrum of moderate complexity be produced, for which probable structures of major ions were known or could be determined; and (3) that a homologous series of compounds be available, some members of which could be exhaustively deuterium labeled. A survey of compounds indicated that these requirements were met by dialkyl malonates, whose principal unimolecular

(4) "Ion-Molecule Reactions in the Gas Phase," *Advan. Chem. Ser.*, No. 58 (1966).

(5) K. R. Ryan, L. W. Sieck, and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

(6) L. W. Sieck, F. P. Abramson, and J. H. Futrell, *ibid.*, **45**, 2859 (1966).

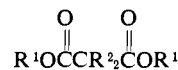
(7) W. Heerma and G. Dijkstra, *Org. Mass Spectrom.*, **3**, 379 (1970).

(8) See also J. L. Franklin, Y. Wada, P. Natalis, and P. M. Hierl, *J. Phys. Chem.*, **70**, 2353 (1966).

(9) For examples and leading references to recent work on proton affinities, see (a) M. A. Haney and J. L. Franklin, *ibid.*, **73**, 4328 (1969); (b) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970); **93**, 3911, 4315 (1971).

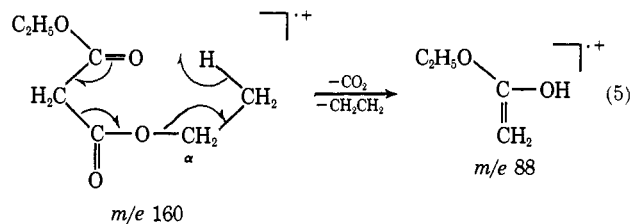
reaction paths were studied by Williams and his collaborators.^{10,11}

Unimolecular Fragmentation Products of Dialkyl Malonates. Mass spectra of compounds 1–9 were



- | | |
|--|--|
| 1a, $\text{R}^1 = \text{CH}_3$; $\text{R}^2 = \text{H}$ | 5a, $\text{R}^1 = n\text{-C}_4\text{H}_9$; $\text{R}^2 = \text{H}$ |
| b, $\text{R}^1 = \text{CH}_3$; $\text{R}^2 = \text{D}$ | b, $\text{R}^1 = n\text{-C}_4\text{H}_9$; $\text{R}^2 = \text{D}$ |
| c, $\text{R}^1 = \text{CD}_3$; $\text{R}^2 = \text{H}$ | c, $\text{R}^1 = \text{CH}_3(\text{CH}_2)_2\text{CD}_2$;
$\text{R}^2 = \text{H}$ |
| 2a, $\text{R}^1 = \text{C}_2\text{H}_5$; $\text{R}^2 = \text{H}$ | d, $\text{R}^1 = \text{CD}_3(\text{CH}_2)_3$;
$\text{R}^2 = \text{H}$ |
| b, $\text{R}^1 = \text{C}_2\text{H}_5$; $\text{R}^2 = \text{D}$ | |
| c, $\text{R}^1 = \text{CH}_3\text{CD}_2$; $\text{R}^2 = \text{H}$ | 6a, $\text{R}^1 = i\text{-C}_4\text{H}_9$; $\text{R}^2 = \text{H}$ |
| d, $\text{R}^1 = \text{CD}_3\text{CH}_2$; $\text{R}^2 = \text{H}$ | b, $\text{R}^1 = i\text{-C}_4\text{H}_9$; $\text{R}^2 = \text{D}$ |
| 3a, $\text{R}^1 = n\text{-C}_3\text{H}_7$; $\text{R}^2 = \text{H}$ | c, $\text{R}^1 = (\text{CH}_3)_2\text{CHCD}_2$;
$\text{R}^2 = \text{H}$ |
| b, $\text{R}^1 = n\text{-C}_3\text{H}_7$; $\text{R}^2 = \text{D}$ | |
| c, $\text{R}^1 = \text{CH}_3\text{CH}_2\text{CD}_2$;
$\text{R}^2 = \text{H}$ | 7a, $\text{R}^1 = \text{sec-C}_4\text{H}_9$;
$\text{R}^2 = \text{H}$ |
| d, $\text{R}^1 = \text{CH}_3\text{CD}_2\text{CH}_2$;
$\text{R}^2 = \text{H}$ | b, $\text{R}^1 = \text{sec-C}_4\text{H}_9$;
$\text{R}^2 = \text{D}$ |
| e, $\text{R}^1 = \text{CD}_3\text{CH}_2\text{CH}_2$;
$\text{R}^2 = \text{H}$ | |
| 4a, $\text{R}^1 = i\text{-C}_3\text{H}_7$; $\text{R}^2 = \text{H}$ | 8a, $\text{R}^1 = n\text{-C}_5\text{H}_{11}$; $\text{R}^2 = \text{H}$ |
| b, $\text{R}^1 = i\text{-C}_3\text{H}_7$; $\text{R}^2 = \text{D}$ | b, $\text{R}^1 = n\text{-C}_5\text{H}_{11}$; $\text{R}^2 = \text{D}$ |
| c, $\text{R}^1 = (\text{CH}_3)_2\text{CHCD}_2$; $\text{R}^2 = \text{H}$ | 9a, $\text{R}^1 = n\text{-C}_5\text{H}_{17}$; $\text{R}^2 = \text{H}$ |
| d, $\text{R}^1 = (\text{CD}_3)_2\text{CH}$; $\text{R}^2 = \text{H}$ | b, $\text{R}^2 = n\text{-C}_5\text{H}_{17}$; $\text{R}^2 = \text{D}$ |

examined and found to follow the general behavior of dimethyl¹¹ (1a) and diethyl malonate¹⁰ (2a). Variation of ion source temperature from 190 to 310°, and of electron energy from 20 to 70 eV, was found to have no significant effect upon reactions leading to the formation of $M + H$ from 2a. All spectra were therefore acquired under uniform conditions suitable for all compounds, 250° and 20 eV. Emphasis in the present study was placed on the *n*-alkyl malonates because of a greater tendency to form $M + H$, and the occurrence of fewer competing reactions in the primary spectrum which might be associated with branching. The identities of the principal alkyl malonate ion types can be discussed in terms of diethyl malonate (2a), whose spectrum is shown in Figure 1, and principal reactions are noted in Scheme I. The primary structures and mechanisms shown are supported by deuterium labeling data from the present study and agree with the earlier postulates,¹⁰ which were not based on deuterium labeling. The exception is m/e 88, earlier proposed by Williams to arise as indicated in eq 5, but shown by our data to con-



tain 75% of the rearranged hydrogen from the α carbon of the C_2 fragment which is lost. Preference for the α hydrogen in this instance reveals the operation of a more complex mechanism but probably leads to the same ion structure as shown above in which the rearranged hydrogen has migrated to oxygen.

Mass spectra of 2b–d reveal that 80% of the total hydrogen transferred to oxygen in the formation of m/e 133 originates in the β position. Transfer of one hy-

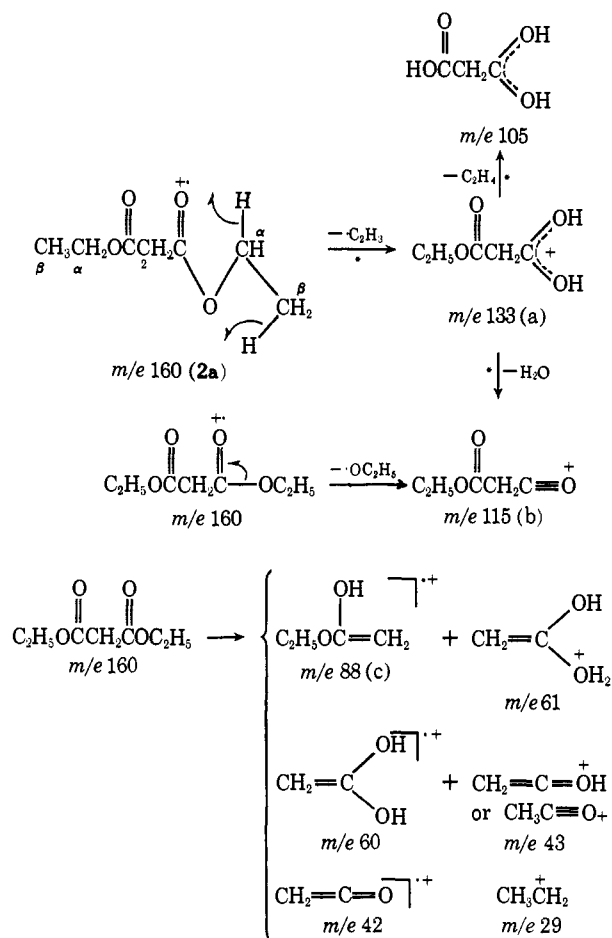
(10) J. H. Bowie, D. H. Williams, S.-O. Lawesson, and G. Schroll, *J. Org. Chem.*, **31**, 1792 (1966).

(11) I. Howe and D. H. Williams, *J. Chem. Soc. C*, 202 (1968).

Table I. Relative Abundances (% Σ_{20}) of Selected Fragment Ions from $\text{ROCOCH}_2\text{CO}_2\text{R}$ at 20 eV (12 eV)

Compd	R ⁺	$\text{ROCOCH}_2\text{C}(\text{OH})_2^+$	$\text{HOCOCH}_2\text{C}(\text{OH})_2^+$	$\text{ROCOCH}_2\text{CO}^+$	$\text{ROC}(\text{OH})\text{CH}_2^+$
1a	2 (5)			33 (21)	20 (37)
2a	12 (9)	17 (39)	1 (1)	22 (7)	10 (15)
3a	17 (2)	3 (9)	26 (50)	19 (12)	1 (2)
4a	18 (14)	2 (5)	18 (28)	14 (10)	4 (12)

Scheme I



hydrogen from the β position by random abstraction of the second¹² could reasonably explain the deviation of this value from the 50% expected from the mechanism shown in Scheme I. The origin of labile hydrogen in m/e 43 is 45% from α and 55% from the β position. Low abundance and interference from adjacent ions preclude accurate measurement of the source of hydrogen in m/e 60, 61, and 105. Variations in electron energy in the range 12–20 eV did not significantly alter the distribution of deuterium in the labeled ions.

Higher alkyl malonates were observed to fragment by the same pathways outlined in Scheme I, but with greatly altered abundances of ions heavier than mass 100. A representative example of these effects is given by the spectrum of diamyl malonate (8a), Figure 2, and in Table I. Fragment ions in Figure 2 which correspond to principal ions of different mass in Figure 1 are designated by a–c as indicated in Scheme I. As the number of favorable decomposition pathways in alkyl malonates increases, molecular ion abundances de-

crease, with the result that no molecular ions are observed in the spectra of 3–9. The relative abundances of the protonated half-ester and acylium ions (corresponding to a and b, Scheme I) decrease with increasing chain length in favor of m/e 105, which is the base peak

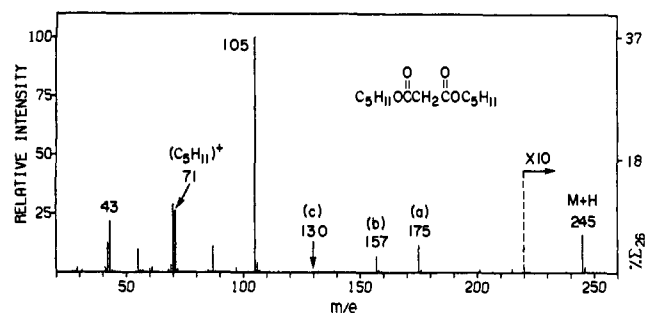
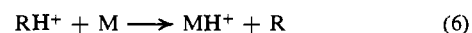


Figure 2. Mass spectrum of diamyl malonate (8a).

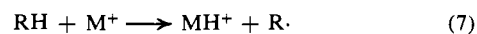
in the spectra of the higher alkyl malonates (e.g., Figure 2). Branching in the alkyl moiety was predictably found to increase the relative abundance of alkyl fragments, and to decrease the extent of rearrangement processes.

Discussion

Intermolecular hydrogen transfer reactions can in principle occur either by proton transfer from a molecular or fragment ion to a neutral molecule (e.g., eq 6) or



by transfer of neutral hydrogen to the molecular ion (eq 7). The low abundance (Figure 1) or absence



(Figure 2) of molecular ions in the mass spectra of alkyl malonates requires that the reaction proceed predominantly by proton transfer, which is the most common mechanism for heteroatom-containing molecules. The majority of the potential precursor ions in Scheme I contain labile hydrogen bound to oxygen. Following the earlier established preference for transfer of labile hydrogens in intermolecular processes,^{5–7} the same preference can *a priori* reasonably be assumed to exist in the formation of $\text{M} + \text{H}$ from dialkyl malonates.

The fraction of hydrogen transferred (F) from each labeled position in the formation of $\text{M} + \text{H}$ is given in Table II. All compounds for which positional data are complete exhibit moderate isotope effects (ΣF) indicating discrimination against transfer of deuterium, and range from 30 (1, 12 eV) to 8% (3, 20 eV). The source of discrimination which is observed can be either during formation of the primary ion spectrum, or during the intermolecular hydrogen transfer reaction. Changes in relative ion abundances upon deuteration in such cases as 2a vs. 2b were found to vary widely, but were

(12) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 184–186.

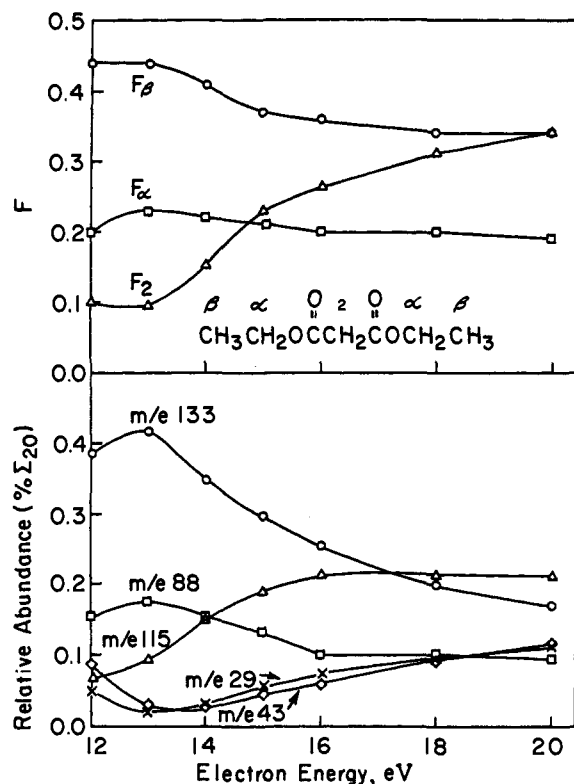


Figure 3. Variations of the fraction of hydrogen transferred (F) to form $M + H$ from each position (upper panel) compared with relative abundances of major ions (lower panel), as a function of electron energy in the mass spectrum of **2**.

generally in the range 5–15%. The isotope effects shown by ΣF values in Table II therefore undoubtedly contain significant contributions from the primary ion spectrum, although intermolecular hydrogen-transfer processes must also play a major role.

Table II. Positional Hydrogen Transfer Fractions for Formation of $M + H$ from Dialkyl Malonates

Compd	Position	(M + D)	
		(M + D) + (M + H) 12 eV	20 eV
1b	2	0.26	0.48
1c	α	0.44	0.36
		ΣF 0.70	0.84
2b	2	0.10	0.34
2c	α	0.20	0.19
2d	β	0.44	0.34
		ΣF 0.74	0.87
3b	2	0.16	0.36
3c	α	0.10	0.10
3d	β	0.29	0.19
3e	γ	0.36	0.27
		ΣF 0.91	0.92
4b	2	0.20	0.37
4c	α	0.15	0.10
4d	β	0.50	0.41
		ΣF 0.85	0.88
5b	2	0.11	0.22
5c	α	0.10	0.09
5d	δ	0.10	0.08
6b	2	0.19	0.27
6c	α	0.15	0.11
7b	2	0.24	0.36
8b	2	0.04	0.12
9b	2	0.03	0.03

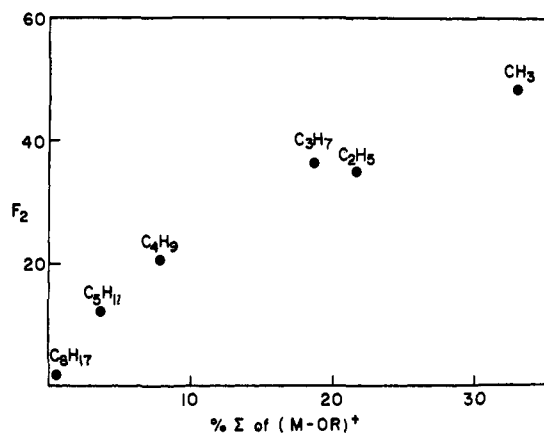


Figure 4. Variation of the fraction of hydrogen transferred from C-2 (F_2) to form $M + H$ as a function of acylium ion abundance in the mass spectra of n -alkyl malonates.

Strong evidence for the identities of some precursors is gained from Figure 3. The abundance of m/e 133, which bears labile hydrogen principally from the β position, closely parallels the change in the fraction of hydrogen transferred from the β position (F_β) as a function of electron energy, and thus must be considered a highly likely precursor. Similar correspondence exists between m/e 115 and F_2 , which on the basis of recent work by Djerassi,¹³ McLafferty,¹⁴ and their coworkers, probably retains the keto form, and therefore involves transfer of hydrogen from carbon (C-2). The abundance of mass 88 shows variation similar to F_α , in accordance with the high percentage of labile hydrogen transferred from C- α in the initial formation of m/e 88. Other important evidence regarding m/e 88 comes from the spectrum of **1a** (see Table I) in which the analogous ion (m/e 74) is abundant. The intensity of the mass 74 peak was found to decrease from 37% Σ_{15} at 20 eV to 20% Σ_{15} at 12 eV in parallel to a change in F_α from 0.44 to 0.36, and was the only abundant ion in the spectrum of **1a** to diminish with increasing voltage. No correlation is apparent for m/e 43, possibly due to the multiple origins of its labile hydrogen, as previously discussed. The absence of a definite correlation for m/e 29 in Figure 3 is also reasonable, since the ion bears no heteroatom-bound hydrogen.¹⁵

Further evidence for the relationship between the acylium ion (ion type b, Scheme I) and the activity of hydrogen at C-2 was found by comparing the fraction of hydrogen transferred from C-2 to form $M + H$ with acylium ion abundances from the mass spectra of different compounds. The results, shown in Figure 4, indicate a smooth rise in F_2 with acylium ion abundance, in support of the latter ion's participation as a precursor to $M + H$. Acylium ions are also prominent in the spectra of branched chain malonates (**4**, **6**, **7**), which show hydrogen transfer from C-2 (Table II). Although other ions are present which contain hydro-

(13) G. Eadon, J. Diekman, and C. Djerassi, *J. Amer. Chem. Soc.*, **92**, 6205 (1970).

(14) F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfield, *ibid.*, **93**, 3720 (1971).

(15) However, although the present study indicates that oxygen-bound protons are readily transferred, alkyl ions are also valid proton donors, as recently demonstrated in the case of propyl ions.¹⁶

(16) D. J. McAdoo, F. W. McLafferty, and P. F. Bente III, *J. Amer. Chem. Soc.*, **94**, 2027 (1972). We thank Professor McLafferty for making this manuscript available to us prior to publication.

gen from C-2, none in Scheme I appear structurally likely to be efficient donors of the C-2 hydrogen.

On the basis of the foregoing data, the protonated dicarboxylic acid ions $\text{HOCOCH}_2\text{C}(\text{OH})_2^+$ (m/e 105) should be as efficient as their parents ($\text{ROCOCH}_2\text{C}(\text{OH})_2^+$) as donors of protons which originate in the alkyl moiety. As shown in Table I, the abundance of m/e 105 increases with chain length in the series 1a–3a. In the spectrum of di-*n*-propyl malonate (3a) the principal ions are C_3H_7^+ , $\text{C}_3\text{H}_7\text{OCOCH}_2\text{CO}^+$, and m/e 105, of which the latter can reasonably be assumed to be the best potential donor of alkyl group protons. If for each alkyl position the percentage of rearranged deuterium is compared with the corresponding fraction of hydrogen (deuterium) transferred to form $\text{M} + \text{H}$, a strong correlation is obtained, as shown in Figure 5. The apparent linearity of the correlation further suggests that m/e 105 is a much more effective donor of alkyl group protons than any of its competitors. Further evidence for the participation of m/e 105 is gained from the magnitudes of F_α and F_β for compound 5 (Table II). In addition, the low values of F_α for 4c and 6c in Table II correspond to low deuterium contents of $\text{HOCOCH}_2\text{C}(\text{OH})_2^+$ in their spectra. Since β and γ hydrogens are preferentially transferred in the formation of ions of this type,¹² the low values of F_α and F_β concur with the identity of m/e 105 as an active transfer agent of alkyl protons.

Participation of other ions as effective proton donors cannot be completely excluded, although no further data in support of their reactivity are available from the present study. Ion cyclotron double resonance experiments,¹⁷ using compound 2a as a substrate, indicated m/e 133, 88, 145, 61, 43, and 29 as participants in $\text{M} + \text{H}$ formation, although the magnitudes of the signals obtained were all relatively low. The identity of the proton which is transferred from the minor ion m/e 145 cannot be determined from our data. The apparent inertness of m/e 60 (Scheme I) is somewhat surprising in view of the activity of m/e 88, although the data are not conclusive.

In systems which show a strong tendency to form $\text{M} + \text{H}$ ions the question arises as to whether $\text{M} + \text{H}$ further decomposes to generate fragment ions which would comprise a spectrum of secondary ions. The observed result would be changes in the observed recorded pattern of relative ion intensities, and possibly the appearance of new peaks. In the present case no such alterations were observed when using 2a as a model at pressures sufficient to produce $\text{M} + \text{H} = 4\% \Sigma_{20}$. Further experiments were carried out in a binary system composed of 2a and 50-fold excess CD_3I , which was found to be a highly effective deuterium donor. Although a significant $\text{M} + \text{D}$ peak ($2\% \Sigma_{20}$) was formed from 2a, no changes in the relative intensities of the major fragment ions or their first isotope peaks were observed, indicating the absence of intermolecularly transferred hydrogen in any of the fragment ions. Likewise, no evidence was found for bimolecular dehydration reactions of ions which contain a labile proton on oxygen, as has been previously reported for aliphatic alcohols.¹⁸ The apparent failure of $\text{M} + \text{H}$ species to fragment is interesting, since the

(17) We are grateful to Dr. Robert Wilcox of Varian Associates, Palo Alto, Calif., for making these measurements.

(18) J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969).

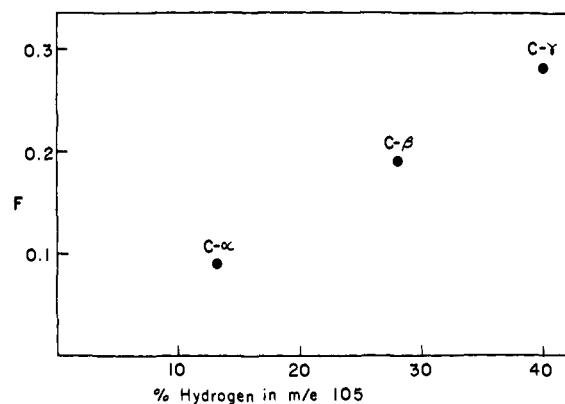


Figure 5. Comparison for each alkyl carbon, of the fraction of hydrogen (F) transferred to form $\text{M} + \text{H}$ with the percentage alkyl hydrogen in the m/e 105 ion from the mass spectrum of 3.

stabilization of $\text{M} + \text{H}$ through ion–molecule collisions should not play a major role here as it does in chemical ionization¹⁹ mass spectrometry.²¹ However, the question must still remain open, and awaits further investigation with other model systems having large reaction cross sections for the formation of $\text{M} + \text{H}$ ions.

Experimental Section

Mass spectra were recorded on an LKB 9000 instrument, using either reservoir or gas chromatographic (6 ft, 1% OV-17) inlet systems. Data were acquired at ion source and carrier gas separator temperatures of 250° and at electron energies of 20 eV unless stated otherwise. Sample sizes in the range 20–30 μl (reservoir), or 10–30 μg (gas chromatograph) were used, which was usually sufficient to produce response of the ionization gauge mounted externally to the ion source housing, but insufficient to cause pressure broadening effects in the recorded mass spectrum.

Dimethyl malonate (1a) and diethyl malonate (2a) were commercial samples and were gas chromatographically pure. Ethanol-1,1- d_2 , ethanol-2,2,2- d_3 , 2-propanol-1,1,1,3,3,3- d_6 , and 2-propanol-2- d used in preparation of labeled esters, and methyl- d_3 iodide were obtained from Merck Sharp and Dohme of Canada, Ltd. 1-Propanol-1,1- d_2 , 1-butanol-1,1- d_2 , and 2-methyl-1-propanol-1,1- d_2 were prepared by LiAlD_4 (Merck) reduction of the appropriate acids or ethyl esters. Propanol-2,2- d_2 was obtained by LiAlH_4 reduction of propionic-2,2- d_2 acid, which was prepared by the method of Atkinson, *et al.*²² Butanol-4,4,4- d_3 was made by reaction of the Grignard reagent from $\text{CD}_3\text{CH}_2\text{Br}$ with ethylene oxide. 1-Propanol-3,3,3- d_3 was prepared analogously from methyl- d_3 iodide and ethylene oxide.

With the exception of 1a, 2a, and the b series, malonate esters were prepared by addition of redistilled malonyl chloride to an ethereal solution of the appropriate alcohol. After neutralization of excess acid and extraction with water, the esters were dried over CaCl_2 . Distillation was in general not necessary but was carried out whenever possible. Introduction of a deuterium label at C-2 (1b–9b) was effected by stirring the ester with $\text{D}_2\text{O}-\text{Na}_2\text{CO}_3$, and the ester layer dried over CaCl_2 . Further purification of products was not attempted; those labeled esters which were not gas chromatographically homogeneous were introduced into the mass spectrometer as single components after passage through the gas chromatographic inlet system.

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(19) By contrast, in the methane chemical ionization spectrum of 2a (0.5 Torr), the principal fragment ion m/e 133 retains a large fraction of the proton initially transferred from CH_5^+ , as shown by experiments using CD_4 as reagent gas.²⁰

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