Electron Impact Studies. Part 119.[1] The Nature of the Transition State for Loss of Keten from Quinone Acetate Molecular Anions. A Kinetic Isotope Effect Study

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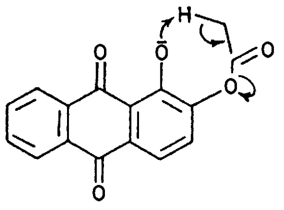
A combination of relative rates of reaction, primary deuterium isotope effects, and kinetic energy release values (for metastable decompositions) suggests that the unimolecular elimination of keten from quinone acetate radical anions proceeds *via* a rate-determining step which possibly involves hydrogen atom transfer to a phenoxide radical centre. The reaction is ' endothermic,' *i.e.* the unsymmetrical transition state resembles the product of the reaction.

It would be predicted from the quasi-equilibrium theory of mass spectrometry [2,3] (which has been shown to hold for negative ions in particular cases [4]) that low-energy anions (produced by thermal or secondary electron capture [5-10]) should yield primary deuterium isotope effects, *if* suitable decomposition channels involving hydrogen loss or transfer are available. This prediction has led us to consider the possible application of deuterium isotope effects as a mechanistic probe for the reactions of negative ions in the gas phase.



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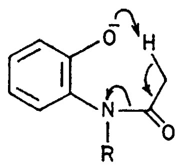
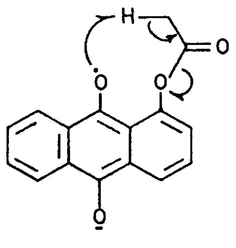
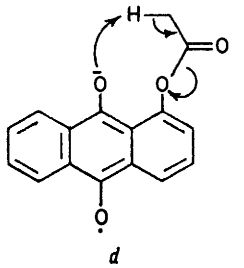


b



c



d

Reactions involving hydrogen loss or transfer in the negative mode are rare; one which has been reported is the unimolecular elimination of CH_2CO from both *odd-* and *even-electron* anions derived from aromatic acetates or acetamides containing *o*-oxygen substituents.[11,12] In this context, we have reported [13] that primary deuterium isotope effects for *proton* transfer reactions accompanying keten loss from decomposing *anions* of types *a* and *b* range from 2.1 to 2.5 for decompositions occurring in the first field-free region of the mass spectrometer. In addition, it appears that the transition state is asymmetric (with respect to $\mathrm{O\cdots H\cdots C}$) and that the $\mathrm{O\cdots\widehat{H}\cdots C}$ bond angle lies between 90 and 120°.[13]

In the case of loss of keten from a *radical anion*, the reaction can be depicted as either a hydrogen atom transfer (*c*, in the case of the 1-acetoxyanthraquinone molecular anion), or a proton transfer *d*. Of the two, the hydrogen atom transfer is the more plausible, since homolytic cleavage of a C–H bond is energetically more favoured than heterolytic cleavage.†

In this paper, we consider in detail, the losses of keten and methylketen from quinone acetate and propionate molecular anions.

RESULTS AND DISCUSSION

We first chose to study the 1-acetate and 1-propionate of anthraquinone together with the analogous 2- and 8-substituted 1,4-naphthaquinones, since these systems have the ester group *peri* or *ortho* to a quinone oxygen. Their negative-ion mass spectra show only molecular ions and fragment ions produced by the decomposition

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† The bond energy of the C–H bond in methane is 104 kcal mol^{-1}, whereas the heat of formation of H^+ from various hydrocarbons is in excess of 300 kcal mol^{-1}.[14] However, for this work we are dealing not with simple alkyl radicals or carbanions, but with such species stabilised by a carbonyl group. Figures for such dissociation energies are not available, so the mode of cleavage must remain in doubt. We believe the results here presented, interpreted on the basis of hydrogen atom dissociation, lend credence to this assumption.

[1] Part 118, J. H. Bowie, *Austral. J. Chem.*, 1977, **30**, 2161.

[2] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci. U.S.A.*, 1952, **38**, 667.

[3] H. M. Rosenstock, *Adv. Mass Spectrom.*, 1968, **4**, 523–547.

[4] C. Lifshitz, A. M. Peers, R. Grajower, and M. Weiss, *J. Chem. Phys.*, 1970, **53**, 4605.

[5] M. von Ardenne, *Z. Angew. Phys.*, 1959, **11**, 121.

[6] M. von Ardenne, K. Steinfelder, and R. Tümmler, ' Electronenanlagerungs Massenspectrographie organischer Substanzen,' Springer Verlag, New York, 1972.

[7] C. L. Brown and W. P. Weber, *J. Amer. Chem. Soc.*, 1970, **92**, 5775.

[8] T. McAllister, *J.C.S. Chem. Comm.*, 1972, 245.

[9] J. H. Bowie and A. C. Ho, *Austral. J. Chem.*, 1973, **26**, 2009.

[10] L. G. Christophorou, A. Hadjiantiou, and J. G. Carter, *J.C.S, Faraday II*, 1973, 1713.

[11] A. C. Ho, J. H. Bowie, and A. Fry, *J. Chem. Soc.* (*B*), 1971, 530.

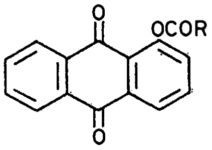
[12] J. H. Bowie and A. C. Ho, *Austral. J. Chem.*, 1971, **24**, 1093.

[13] J. A. Benbow, J. C. Wilson, and J. H. Bowie, *Internat. J. Mass Spectrometry Ion Phys.*, in the press.

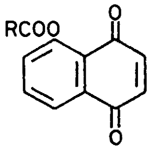
[14] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, ' Ionization Potential, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' NSRDS–NBS 26, United States Department of Commerce, 1969, p. 14.

$M^{-\cdot} \longrightarrow (M - \text{RCHCO})^{-\cdot}$ (R = H or Me).[11,12]* The compounds used for this study were (1)—(18).

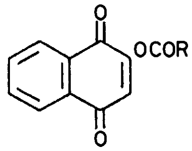
The spectra of the [$^2H_2$]propionates (5), (11), and (17) show the exclusive fragmentation $M^{-\cdot} \longrightarrow (M - \text{MeCDCO})^{-\cdot}$, demonstrating for propionates that only a hydrogen attached to the carbon α to the propionate carbonyl, may transfer to a quinone oxygen. The transition state for propionates is therefore analogous to that depicted in *c* for acetates.



(1) R = Me
(2) R = CD_3
(3) R = CH_2D
(4) R = Et
(5) R = CD_2Me
(6) R = CHDMe



(7) R = Me
(8) R = CD_3
(9) R = CH_2D
(10) R = Et
(11) R = CD_2Me
(12) R = CHDMe



(13) R = Me
(14) R = CD_3
(15) R = CH_2D
(16) R = Et
(17) R = CD_2Me
(18) R = CHDMe

Table 1 lists the following parameters for the acetates and propionates. (i) The values of the primary deuterium isotope effect ($k_{\text{H transfer}}/k_{\text{D transfer}}$) measured both in the ion source and in the first field-free region of the mass spectrometer. The values were obtained directly from measured peak abundances corrected for ^{13}C isotope peaks [*e.g.* for the two processes $M^{-\cdot} \longrightarrow (M - \text{CHDCO})^{-\cdot}$ (hydrogen transfer) and $M^{-\cdot} \longrightarrow (M - \text{CH}_2\text{CO})^{-\cdot}$ (deuterium transfer) from (3), (9), and (15)]. Peak abundances for decompositions occurring in the first field-free region were measured by the metastable focusing technique.[15,16]

(ii) The ratio of the abundances of the peaks due to the ions $M^{-\cdot}$ and $[M - \text{RCHCO}]^{-\cdot}$. This parameter qualitatively indicates *relative* rates and activation energies.

(iii) Kinetic energy release values for the various losses of RCHCO in the first field-free region from the unlabelled compounds (the $T_{50\%}$ values) and the ratio T_H/T_D [$T_{50\%\,(\text{H transfer})}/T_{50\%\,(\text{D transfer})}$] for the unlabelled and $^2H_3$ (or $^2H_2$) analogues (see footnotes in Table 1). In explanation, when a metastable ion fragments unimolecularly, kinetic (translational) energy (T) is released in the centre of mass, and the resulting range of kinetic energies can be used to calculate the value of T.[17,18] It has been proposed [19,20] that the ion kinetic energy peak width at half height ($T_{(50\%)}$) is a *reasonable* measure of the kinetic energy release, and this parameter has been used in this study. The magnitude of T for a rearrangement reaction of a negative ion often gives an insight into the nature of the transition state for that reaction.[21] For example, when the reverse activation energy of the reaction is large (say 1 eV), a large value of T (say 0.3—1 eV) indicates strong bonding in the transition state. A smaller value of T is due to more effective partitioning of internal energy in the transition state into the effective vibrational modes of the molecule, and is indicative of weaker bonding in the transition state.[18] Variation in T_H/T_D values could show the same overall trend as that of the k_H/k_D values, since both parameters are inter-related by the relative vibrational frequencies [23-25] of the C···H···O and C···D···O bonding in the transition state.

The data listed in Table 1 show the following. (*a*) k_H/k_D Values range between 1.5 and 2.5 (first field free region), *i.e.* the hydrogen transfer is involved in the rate-determining step of the reaction. (b) There is little difference in isotope effects measured for decompositions in the ion source or the first field free region. This seems to be a general feature for negative ions formed by secondary electron capture (*cf.* ref. 13) and is presumably due to uniformly low internal energies of the decomposing ions in both regions. (c) Isotope effects are slightly higher for propionates than acetates perhaps indicating less bonding in the transition state for propionates, due either to an electronic or steric effect of the methyl group of the propionate residue. (d) T Values increase with increasing k_H/k_D indicating increased bonding in the transition state as k_H/k_D increases, and/or increasing symmetry of the transition state as T increases, *i.e.* a situation where the sum of the excess energy and reverse activation energy (*cf.* ref. 22) increase

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* When the ester group is not adjacent to the quinone centre, as for example in 2-acetoxyanthraquinone or 6-acetoxy-1,4-naphthaquinone, the only decomposition noted is $M^{-\cdot} \longrightarrow (M - \text{CH}_3\text{CO}\cdot)^-$.

[15] A. H. Struck and H. J. Major, paper presented at ASTM E14 meeting, Dallas, 1969.

[16] J. H. Bowie and S. G. Hart, *Internat. J. Mass Spectrometry Ion Phys.*, 1974, **13**, 319.

[17] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.

[18] R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam–London–New York, 1973, pp. 57—70.

[19] J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Internat. J. Mass Spectrometry Ion Phys.*, 1972, **8**, 341.

[20] D. T. Terwilliger, J. H. Beynon, and R. G. Cooks, *Proc. Roy. Soc.*, 1974, **A341**, 135.

[21] J. H. Bowie, S. G. Hart, and T. Blumenthal, *Internat. J. Mass Spectrometry Ion Phys.*, 1976, **22**, 7.

[22] Ref. 18, p. 105.

[23] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265.

[24] J. Bigeleisen, *Pure Appl. Chem.*, 1964, **8**, 217.

[25] L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press, New York, 1960.

as k_H/k_D increases. Unfortunately we have no way of estimating either E_{excess} or $E_{reverse}$ for these systems. (e) Variations in T_H/T_D values parallel the variations in k_H/k_D. (f) The relative rate of the rearrangement reaction *increases* with *increasing* isotope effect (from the relative abundance ratios of molecular and fragment peaks).

TABLE 1

Kinetic isotope effect, kinetic energy release, and relative peak abundance data for losses of keten from (3), (9), and (15) and methylketen from (6), (12), and (18)

	$k_{H\ transfer}/k_{D\ transfer}$				
Compound	Source (±0.05)	First field free region (±0.1)	$T_{50\%}$ (eV) [a] (±0.005)	T_H/T_D [b] (±0.1)	$[M^{-\cdot}]/[(M - RCHCO)^{-\cdot}]$ [c]
(3)	1.7	1.8	0.095	1.65	0.21
(6)	1.8	1.9	0.085	2.0	0.27
(9)	2.3	2.45	0.13	2.4	0.05
(12)	2.35	2.5	0.145	2.3	0.05
(15)	1.45	1.5	0.025	1.6	0.43
(18)	1.4	1.55	0.035	1.6	0.51

[a] Measured for the unlabelled compounds (1), (4), (7), (10), (13), and (16). [b] All T values were measured with an accelerating potential of 3.6 kV. The reported values T_H/T_D are *not* those observed for the $^2H_1$ derivatives, since discrepancies due to overlap of peaks 1 a.m.u. apart may occur using the medium energy resolving RMU 7D instrument. The values shown are in fact $T_{(M-CH_2CO)}/T_{(M-CD_2CO)}$ or $T_{(M-MeCHCO)}/T_{(M-MeCDCO)}$ obtained respectively for the appropriate unlabelled and $CD_3CO{\cdot}O$ (or $MeCD_2CO{\cdot}O$) derivatives corresponding to (3), (9), and (15) and (6), (12), and (18). Small differences in the values of zero point energies for the labelled and unlabelled compounds have been ignored. [As justification of this procedure, we have measured the appropriate T values for the metastable dissociations $M^{-\cdot} \longrightarrow (M - CH_3CO\cdot)^-$ from 2-acetoxyanthraquinone and $M^{-\cdot} \longrightarrow (M - CD_3CO\cdot)^-$ from the $CD_3CO{\cdot}O$ analogue. In this case $T_{(M-CH_3CO\cdot)}/T_{(M-CD_3CO\cdot)} = 1.0 \pm 0.1$]. [c] Abundances were obtained from the spectra of the unlabelled compounds.

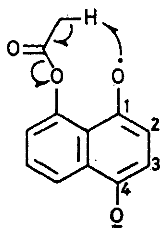
In general, an increase in k_H/k_D accompanies increases in T, T_H/T_D, and in the rate of reaction (*decreases* in the activation energy of the process).

Before dealing with (i) the implications of the above observations and (ii) the large difference in isotope effect noted for the 2- and 8-substituted naphthaquinones, it is necessary to summarise briefly current knowledge of isotope effects for hydrogen transfer transition states. This work pertains primarily to reactions in solution, but should equally well hold for gas-phase reactions of the type $HX + Y\cdot \longrightarrow HY + X\cdot$.

The primary deuterium isotope effect varies with the symmetry of the transition state, is a maximum when the hydrogen is symmetrically bound to the atoms between which it is being transferred (*i.e.* $X \cdots H \cdots Y$), and in the limiting case of a highly asymmetric transition state, the isotope effect approaches unity.[23-26] The isotope effect is a maximum for a linear transition state ($X \cdots H \cdots Y$ and decreases as the angle $X \cdots \hat{H} \cdots Y$ decreases.[27] The occurrence of such maxima has been theoretically justified [28] and experimentally observed for both proton [29-31] and hydrogen atom [26] transfer reactions. The most symmetrical transition state should occur when the heat of reaction is almost zero; exothermic and endothermic reactions have unsymmetrical transition states resembling reactants and products respectively.[32,33]

Recent publications [34] have described methods which allow for the effects of hydrogen tunnelling in hydrogen transfer reactions in solution; such corrections require a knowledge of the imaginary frequencies along the reaction co-ordinate. Tunnelling is often pronounced when some or all of the following criteria are met, large isotope effects, excessive temperature dependence of isotope effects, symmetrical transition states, curved Arrhenius plots, and unexpectedly high rates of reaction. The gas-phase reactions that we are considering in this study have relatively low isotope effects and unsymmetrical transition states, and we have therefore ignored any possible tunnelling contributions.

The data in Table 1 show that for the rearrangements studied, the isotope effect generally increases as the energy of activation E_a decreases. This suggests endothermic reactions, with 'product like' transition states, *i.e.* the reactions lie on the 'product' side of the maximum of the Bell [30,31] curve (the plot of k_H/k_D against reaction co-ordinate). This can only be a hypothesis since the results recorded in Table 1 are derived from three quite different systems, each of which may have different symmetry and electronic requirements for the transition state. A single system is therefore required for study in which the change in transition state parameters can be monitored as a function of a single variable, *e.g.* the radical character of the hydrogen acceptor site in the decomposing molecular anion.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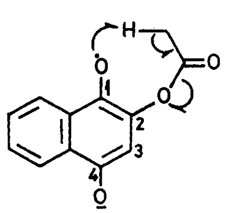
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The system chosen for study must also provide a rationale for the very different isotope effects noted for 8- and 2-acetoxy-1,4-naphthaquinone. If we assume

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[26] W. A. Pryor and K. G. Kneipp, *J. Amer. Chem. Soc.*, 1971, **93**, 5584 and references cited therein.

[27] R. A. M. O'Ferrall, *J. Chem. Soc.* (*B*), 1970, 785.

[28] R. A. M. O'Ferrall and J. Kouba, *J. Chem. Soc.* (*B*), 1967, 985.

[29] A. J. Kresge, *Discuss. Faraday Soc.*, 1965, **39**, 49.

[30] J. L. Longridge and F. A. Long, *J. Amer. Chem. Soc.*, 1967, **89**, 1292.

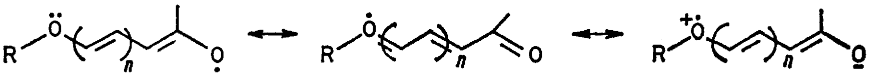
[31] R. P. Bell and B. G. Cox, *J. Chem. Soc.* (*B*), 1970, 194, and references cited therein.

[32] G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

[33] W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, p. 156.

[34] E. S. Lewis, 'Tunnelling in Hydrogen Transfer Reactions,' in 'Proton Transfer Reactions,' eds. E. Caldin and V. Gold, Chapman and Hall, London, 1975.

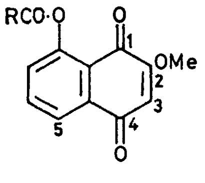
that processes for both compounds involve radical mechanisms (see above), the reactions may be depicted as shown in *e* (k_H/k_D 2.5) and *f* (k_H/k_D 1.5). One obvious difference between *e* and *f* lies in the theoretical stabilization of a radical centre through dipolar contributors [35,36] to the resonance hybrids (Scheme). Such stabilization is supported by an e.s.r. study of methoxy-substituted phenoxyl radicals.[37] This study has shown (i) that there is less electron density at the ring carbons for *o*- and *p*-isomers than for the *m*-substituted species, and (ii) that quinone radical anions can be regarded as phenoxyl radicals with O^- substituents. Such effects are expected to be slightly less with acetoxy-groups.



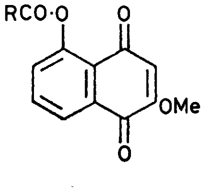
SCHEME

An acyloxy-group would stabilize (by delocalisation) the radical centre at position 1 in *f*, thus effectively stabilizing the reactant (and product) with respect to the transition state. This will *increase* the activation energy (E_a), *increase* the asymmetry of the transition state, and therefore decrease the kinetic isotope effect. In *e*, by constrast, the acyloxy group is incapable of stabilization of the radical centre, hence higher isotope effects would be expected for *e* than *f*.

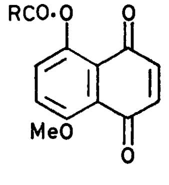
The system chosen to test all the above proposals was 8-acetoxy-1,4-naphthaquinone (see *e*), since this system yields the highest isotope effect for a loss of keten observed in this study. In addition, the ring system has a variety of positions available for additional substitution. We reasoned that the placing of a methoxy-group in different positions with respect to the acetate function should markedly affect the observed isotope effect, since the lone pair of electrons of a methoxy-group will more effectively stabilize a phenoxyl radical than would an acetoxy-group. We expected methoxy-groups at positions 2 and 5 to stabilize the radical centre at position 1, hence reducing the isotope effect for hydrogen transfer when compared with that observed for *e*. In contrast, a methoxy-group at position 3 should not markedly affect the isotope effect since such substitution would stabilize only radical centres at position 4. The compounds (19)—(27) were prepared; the results are summarised in Table 2.



(19) R = Me
(20) R = CD_3
(21) R = CH_2D



(22) R = Me
(23) R = CD_3
(24) R = CH_2D



(25) R = Me
(26) R = CD_3
(27) R = CH_2D

The various values listed in Table 2 are (at least qualitatively) as predicted, and therefore support the proposal that the rearrangement reactions studied may be considered to be endothermic radical reactions with unsymmetrical ' product like ' transition states.

TABLE 2

Kinetic isotope effect, kinetic energy release, and relative peak abundance data for losses of keten from the molecular anions of (9), (21), (24), and (27)

	$k_{H\ transfer}/k_{D\ transfer}$				
Compound	Source (±0.05)	First field free region (±0.1)	$T_{50\%}$ [a] eV (±0.005)	T_H/T_D [b] (±0.1)	$[M^{-\cdot}]/[(M - CH_2CO)^{-\cdot}]$ [a]
(9)	2.3	2.45	0.13	2.4	0.05
(21)	1.45	1.5	0.09	1.65	0.14
(24)	2.1	2.25	0.15	2.2	0.02
(27)	1.55	1.65	0.12	1.75	0.15

[a] Measured using the unlabelled compounds (7), (19), (22), and (25). [b] Measured using the unlabelled compounds and $CD_3CO{\cdot}O$ analogues (8), (20), (23), and (26) (*cf.* footnote *b* in Table 1).

A possible complication that we had anticipated was that a methoxy-group in the 2- or 5-positions could aid the *radical* reaction by a ' conjugative ' type mechanism (*e.g.* see *h* for a 2-MeO group). Such an influence would decrease E_a, making the transition state more symmetrical, thus *increasing* the isotope effect. The isotope effect is markedly *decreased* for 2- and 5-substituents (see above and Table 2), hence stabilization of the radical centre in reactant and product is more important than any directional influence of the type shown in *h*.

In all the above arguments we have assumed radical mechanisms for all reactions and the available evidence points in this direction. Indeed, in the cases of 2- and 5-methoxy-8-acetoxy-1,4-naphthaquinone (low isotope

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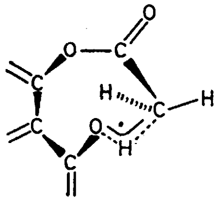
[35] S. F. Nelson in ' Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973 vol. 2, pp. 527—595.

[36] G. A. Russell in ' Free Radicals,' ed. J. K. Kochi, Wiley–Interscience, New York, 1973, vol. 1, p. 305.

[37] W. T. Dixon, M. Moghimi, and D. Murphy, *J.C.S. Faraday II*, 1974, 1713.

effects) we regard the evidence in favour of the radical mechanism to be conclusive, since the effect of a methoxy-group on a phenoxide anion intermediate would be negligible, irrespective of the position of that methoxy-group. We concede however, that in cases of eliminations with higher isotope effects ($k_H/k_D > 2.1$) that there is a possibility of proton transfer, since there is no circumstantial evidence in favour of a radical intermediate. We do not favour a dual mechanism; unfortunately there is no unequivocal evidence to enable complete exclusion of such a possibility.



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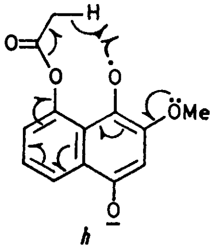

h

EXPERIMENTAL

Mass spectra were measured with an Hitachi–Perkin-Elmer RMU 7D mass spectrometer, modified as described previously.[16] Samples were introduced through an all-glass inlet system maintained at 150°. Spectra were determined using source pressures of 1—2 × 10^{-6} Torr, with V 3.6 kV and E 360 V. The metastable focusing technique (electric sector voltage variation) has been described previously.[16] Kinetic energy release values were measured for peak maxima occurring at 3.6 kV, by automatic accelerating voltage variation, as reported earlier.[21] T Values were determined by the method of Beynon[17,18] with correction being made for the width of the main beam at 3.6 kV. Isotope effects and kinetic energy release values listed in Tables 1 and 2 are average values determined from ten individual measurements in each case. The errors quoted were the ***maximum*** errors obtained for the ten measurements.

All unlabelled acetates and propionates were prepared in almost quantitative yield by the reaction between the appropriate phenol (all are known compounds) and acetic or propionic anhydride with a drop of perchloric acid. All acetates and propionates were crystallised from benzene–light petroleum (b.p. 30—40°) as yellow needles.

Labelled Compounds.—(A) *Precursor anhydrides*. [$^2H_6$]-Acetic anhydride (100%D) was commercially available, and [αα′-$^2H_2$]acetic anhydride (99%D) was prepared by a reported procedure.[38] The reaction between [αα-$^2H_2$]-propionic acid[39] (99%D) and dicyclohexylcarbodi-imide (DCC) (same procedure as used for the labelled acetic anhydride[37]) yielded [$^2H_4$]propionic anhydride (98%D) in 80% yield. [α-$^2H_1$]Propionic acid (99%D) was prepared from α-bromopropionic acid by exactly the same procedure[40] used for [$^2H_1$]acetic acid, and reaction[38] of the acid with DCC gave [αα′-$^2H_2$]propionic anhydride (98%D) in 88% yield.

TABLE 3

Physical and analytical data for new compounds

Compound	M.p. (°C)	Com- position	Found C (%)	Found H (%)	Calc. C (%)	Calc. H (%)
8-Acetoxy-2-methoxy-1,4-naphthaquinone (19)	184—185	$C_{13}H_{10}O_5$	63.45	4.0	63.4	4.1
8-Acetoxy-3-methoxy-1,4-naphthaquinone (22)	211—212	$C_{13}H_{10}O_5$	63.45	4.2	63.4	4.1

(B) *Labelled acetates and propionates*. All labelled acetates and propionates were prepared from the appropriate phenol and the required anhydride as described below. *N.B.* We have described[38] the scrambling of label in [αα′-$^2H_2$]acetic anhydride under basic conditions (presumably through the enol form); the same problem occurs for acidic conditions. For example, if the reaction mixtures from hydroxyquinones and [$^2H_2$]acetic or [$^2H_2$]propionic anhydride are allowed to stand for 1 min after the addition of perchloric acid, the incorporation of label in the product ester is 90—95 for acetates and 80—85% for propionates (the rates of formation of propionates are slower than those of acetates). The following procedure must be adopted to restrict scrambling in the precursor anhydrides prior to esterification.

To the hydroxyquinone (100 mg) suspended in the appropriate anhydride (1 cm^3) is added 1 drop of perchloric acid. Water (5 cm^3) is added *within* 5 s *of the addition of perchloric acid*, and the resulting solid is chromatographed on a preparative silicic acid t.l.c. plate eluting with benzene–ethyl acetate (95 : 5). Yields are generally 50—60 for acetates and 10—25% for propionates. In all cases the retention of label was >97%.

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