Direct *vs.* Indirect Mechanisms in Organic Electrochemistry. Estimates of Activation Energies for Hydrogen Atom Transfer Processes of Relevance in Indirect Mechanisms Using the Bond Energy — Bond Order (BEBO) and Equibonding Methods

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Activation energies for a number of hydrogen abstraction reactions of interest in mechanistic organic electrochemistry have been calculated using the bond energy — bond order (BEBO) and equibonding method. The main emphasis has been put on processes with bearing on the problem of deciding between direct and indirect mechanisms in anodic oxidation, *viz.* acyloxylation, hydroxylation, methoxylation, nitrooxylation, cyanation, carbomethoxylation and azidation. The results indicate that indirect mechanisms might play a more important role than presently assumed.

One of the primary problems in elucidating the mechanism of an organic electrode process is to determine the nature of the electroactive species.[1,2] At the anode, this problem can be formulated as distinguishing between electron transfer (ET) from the substrate (R-H; a direct mechanism) or the anion of the supporting electrolyte (X⁻; an indirect mechanism) being the initial step (eqn. 1 *vs.* 2) of the reaction sequence.

$$R\text{-}H \xrightarrow{-e} [R\text{-}H]^{\cdot +} \qquad (1)$$

$$X^- \xrightarrow{-e} X^{\cdot} \qquad (2)$$

In the former case the follow-up reactions would be dependent upon the reactivity of the radical cation formed (eqn. 1) *vs.* X^{-3-6} whereas in the latter case the free-radical reactivity of $X^{\cdot}$ *vs.* RH would be the decisive factor. Generally one has

attacked this problem by a combination of voltammetry and preparative constant potential electrolysis (CPE), assuming that the demonstration of product formation at a potential where only one of the components is oxidized (and this potential should be lower than that required for oxidation of the second component) is evidence enough for either pathway. It has, however, been pointed out [7,8] that this type of evidence is not wholly unambiguous since adsorption of either component might cause a change in mechanism; this point has received some support by the finding that alkanecarboxylates, with anodic oxidation potentials above *ca* 2.1 V *vs.* SCE can be smoothly oxidized by tris-(4-bromophenyl)aminium ion in an electrocatalytic process, $E_{\frac{1}{2}}$ of the latter species being *ca.* 1.4 V.[9]

Moreover, truly ambiguous cases still do exist simply due to the fact that RH and X⁻ are oxidized at potentials too close to each other ($\Delta E_{\frac{1}{2}} \langle 0.2$ V) causing difficulties of interpretation. The anodic α acetoxylation/nitrooxylation of alkylaromatics in HOAc/NO₃⁻ media is such a case.[10] Finally, several radicals of interest are too unstable for meaningful experimental studies of their reactivity to be performed. Carboxylate radicals, RCOO·, constitute examples of this class because of their high reactivity toward decarboxylation (Table 1).

Against this background it was desirable to use non-experimental methods for estimating the reactivity of X· *vs.* RH, especially since many of the X· of interest in anodic chemistry have been little studied experimentally in homogeneous systems.

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Table 1. Estimated rate parameters for the decarboxylation of acyloxy and alkoxycarbonyl radicals. Unless otherwise stated, references are given in Ref. 1, p. 59.

Radical	Rate constant/s^{-1} (temperature/°C)	E_a/ kcal mol^{-1}	Estimated rate constant at 20 °C
$CH_3COO^{\cdot}$	1.6×10^9 (60)	6.6	4×10^8
$CH_3COO^{\cdot}$ [11]	$>2 \times 10^7$ (25)	<8.5	$>2 \times 10^7$
$(CH_3COO^{\cdot})_{ads}(Pt)$ [12]		16.5	25
$CF_3COO^{\cdot}$ [12]	$(7-700) \times 10^6$ (25)	6.4−9.1	$\sim 10^8$
$(CF_3COO^{\cdot})_{ads}(Pt)$ [12]	50 (25)	16	50
$PhCOO^{\cdot}$ [13]	$(1-3) \times 10^8$ (130)	13.6	2.5×10^7
$PhCOO^{\cdot}$	10^4 (80)	15.4	10^2
$PhCOO^{\cdot}$		18	1
$PhCOO^{\cdot}$ [11]	$<2.5 \times 10^5$ (25)	>11.1	
$^-O_2CCHODCHODCOO^{\cdot}$ [14]		7.5	
$Me-OCO^{\cdot}$	10^{10} (356)	10	10^6
$t\text{-}Bu-OCO^{\cdot}$		7.7	105

Recently we reported a preliminary study[10] on the estimation of the reactivity (as activation energies, E_a) of $NO_3^{\cdot}$ and a few other radicals in hydrogen atom abstraction reactions by the so-called equibonding method developed by Zavitsas.[15] Since this reaction type (eqn. 3) can be expected to be a major one in any reaction that

$$R\text{-}H + X^{\cdot} \rightarrow R^{\cdot} + HX \qquad (3)$$
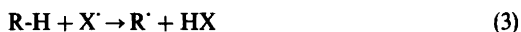
follows an indirect mechanism we have extended these calculations to a number of radical and substrate types prevalent in anodic chemistry. The calculations have now been made by both the equibonding method and the original bond energy-bond order (BEBO) method,[16] as recently modified by Gilliom.[17]

In this paper, Gilliom showed that with the same set of input data the modified BEBO method agrees with experimental activation energies to within ± 1.3 kcal mol^{-1} and the equibonding method to within ± 1.5 kcal mol^{-1}.*

RESULTS

Both the BEBO and equibonding method are based upon the use of Morse potentials for the participating bonds (here R-H and H-X) and for the bond between the two loci of the H atom (here R-X). The required input data in both models are bond

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* 1 kcal = 4.184 kJ.

dissociation energies (D_o), bond lengths (r_e) and IR stretching frequencies (ω_o) for R-H, H-X and R-X. Both methods have been well described in the literature[15−17] and no further elaboration is necessary here, except for noting a small correction in the mathematical expressions to be used (see section on data and calculations). This introduces a small difference (0.1−0.2 kcal mol^{-1}) between E_a values given in this paper and those reported earlier, but has no practical consequences.

Calculated E_a values, using both the BEBO and equibonding method, for a large number of systems of particular interest in electroorganic chemistry, are given in Table 2. The set of X$^{\cdot}$ includes acyloxy radicals, hydroxy, methoxy, nitrate and perchlorate radical as representatives of O−H bond forming systems, cyano, methyl and methoxycarbonyl radical as representatives of C−H bond forming systems and azide radical as the single example of an N−H bond forming system. Among the substrates are included a few aliphatic hydrocarbons, mainly for purpose of calibration, and a number of compounds for which discussions of the problem of direct *vs.* indirect mechanism have been and still are pertinent.[1,2]

It is first necessary to comment somewhat upon the differences between the two sets of calculated E_a values, and the differences between calculated and experimental ones. As can be seen by close inspection of Table 2 the equibonding method gives a larger span of E_a values for each series than the BEBO method; it also differs by sometimes giving negative E_a values which the BEBO method does

Table 2. Calculated (BEBO and equibonding method) and experimental activation energies for hydrogen atom transfer reactions.

No.	Radical/substrate	Activation energy/kcal mol^{-1}		
		BEBO	Equi-bonding	Experimental mean[a]
HCOO˙ +				
1	CH_3-H	11.2	12.4	
2	C_2H_5-H	8.0	10.1	
3	Me_2CH-H	6.4	8.6	
4	Me_3C-H	5.3	7.8	
5	$PhCH_2-H$	4.0	5.6	
6	$HCON(CH_3)CH_2-H$	2.2	1.6	
CH$_3$COO˙ +				
7	CH_3-H	8.9	10.1	
8	C_2H_5-H	6.3	8.2	
9	Me_2CH-H	5.1	6.9	
10	Me_3C-H	4.2	6.2	
11	Allyl$-H$	2.9	2.8	
12	$PhCH_2-H$	3.4	4.2	
13	$HCON(CH_3)CH_2-H$	1.9	1.5	
PhCOO˙ +				
14	CH_3-H	12.3	12.0	
15	C_2H_5-H	8.5	9.2	
16	Me_2CH-H	6.6	7.6	
17	Me_3C-H	5.3	6.7	
18	$PhCH_2-H$	3.8	4.3	
19	$HCON(CH_3)CH_2-H$	2.2	1.5	
HO˙ +				
20	CH_3-H	6.4	8.8	7.2
21	C_2H_5-H	4.1	6.1	5.5
22	Me_2CH-H	3.0	4.2	2.9
23	Me_3C-H	2.1	2.6	2.8
24	$PhCH_2-H$	1.8	1.7	1.9
25	$HCON(CH_3)CH_2-H$	1.3	0.6	
CH$_3$O˙ +				
26	CH_3-H	10.6	10.4	11.0
27	C_2H_5-H	6.9	7.8	7.1
28	Me_2CH-H	5.3	6.8	5.2
29	Me_3C-H	3.9	5.5	4.1
30	$PhCH_2-H$	3.2	4.8	
31	CH_3OCH_2-H	3.9	3.7	
32	Me_2NCH_2-H	2.1	1.6	
33	$HCON(CH_3)CH_2-H$	2.4	4.1	
34	Me_2NCO-H	5.7	7.6	
NO$_3$˙ +				
35	CH_3-H	12.0	11.8	
36	C_2H_5-H	8.0	8.7	
37	Me_2CH-H	6.1	7.3	
38	$C_6H_{11}-H$	6.1	7.1	
39	Allyl$-H$	2.6	1.5	5.2
40	$PhCH_2-H$	3.3	3.9	

41	CH_3OCH_2-H	5.5	6.9	
42	CH_3CO-H	2.9	3.1	5.7
43	$HCOCH_2-H$	7.4	7.3	5.7
44	HO_2CCH_2-H	8.3	8.0	7.6
45	$HOCH_2-H$	5.9	7.1	7.6
46	$NCCH_2-H$	6.7	7.2	
47	$HCON(CH_3)CH_2-H$	2.5	3.4	
$ClO_4^{\cdot}+$				
48	C_2H_5-H	10.1	10.6	
49	$C_6H_{11}-H$	7.8	8.6	
50	$PhCH_2-H$	4.2	5.0	
51	$NCCH_2-H$	8.6	9.1	
52	$HCON(CH_3)CH_2-H$	3.2	4.5	
$CN^{\cdot}+$				
53	CH_3-H	15.0 (11.1)	21.8	2.0^{20}
54	C_2H_5-H	14.2 (7.7)	22.7	0^{20}
55	Me_2CH-H	12.8 (6.2)	20.6	
56	Me_3C-H	11.7 (4.4)	19.2	
57	$PhCH_2-H$	11.2 (4.6)	18.7	
58	Me_2NCH_2-H	8.1	12.1	
$CH_3^{\cdot}+$				
59	CH_3-H	14.6	14.2	14.1
60	C_2H_5-H	11.0	10.7	11.1
61	Me_2CH-H	9.7	9.9	10.0
62	Me_3C-H	8.0	8.0	7.8
63	$C_6H_{11}-H$	9.7	9.4	8.7
64	$Allyl-H$	7.5	7.4	7.8
65	$PhCH_2-H$	7.2	7.4	8.4
66	CH_3OCH_2-H	8.8	8.7	9.7
67	CH_3CO-H	6.3	5.5	7.5
68	$HCOCH_2-H$	10.5	9.6	
69	HO_2CCH_2-H	11.3	10.3	10.2^{21}
70	$HOCH_2-H$	9.3	9.3	9.3
71	$NCCH_2-H$	9.1	7.4	10.0^{21}
72	$HCON(CH_3)CH_2-H$	6.4	6.8	8.3^{21}
73	Me_2NCO-H	9.9	10.4	
$H_3COCO^{\cdot}+$				
74	CH_3-H	22.0	24.7	
75	$PhCH_2-H$	9.1	9.0	
$N_3^{\cdot}+$				
76	CH_3-H	23.8	25.2	
77	C_2H_5-H	18.5	20.8	
78	Me_2CH-H	15.5	18.4	
79	Me_3C-H	13.0	16.8	
80	$C_6H_{11}-H$	15.5	17.8	
81	$PhCH_2-H$	10.3	13.4	
82	$Allyl-H$	9.7	10.3	

[a] Unless otherwise stated, literature references are given in Refs. 10 and 17.

not. There is no over-all valid correlation between the two sets of values.

For cyano radical, with the unpaired electron delocalized over both the carbon and nitrogen atom, two modes of attack upon the hydrogen atom are possible. E_a values based upon attack *via* the carbon atom turn out to be unrealistically large due to the high bond dissociation energy of the C−CN bond which has a large influence on the magnitude of the triplet repulsive term. Good calculations for the second mode of attack, *via* N, were not possible since the relevant data for isonitriles were not available. E_a values for this process were instead simulated by the corresponding amino radical reactions and are given within parentheses in Table 2. With the inherent uncertainties of this approximation in mind we can see that attack *via* N gives consistently lower calculated E_a values, although not nearly as low as the experimental ones. Some reservation should be attached to these, however, since photocyanation studies of aliphatic hydrocarbons [18] indicate that the cyano radical reacts slower with C−H bonds than the chloro atom ("only" HCl formed). For methane, E_a for CN⋅ attack would then be > 3.9 kcal; if we assume that $< 5\%$ HCN would remain undetected in the HCl that is predominantly formed, E_a would be at least 5.6 kcal mol^{-1}.[19]

Anodic formyloxylation. The formyloxy radical appears to be considerably less susceptible toward decarboxylation than the acetoxy radical as judged by its heat of decarboxylation, -6 *vs.* -17 kcal mol^{-1} for $CH_3COO⋅$. From a comparison between the heats of decarboxylation for acyloxy radicals and the corresponding E_a values one can estimate [12] that E_a for decarboxylation should be > 16 kcal mol^{-1}.

Anodic formyloxylation is a relatively little studied process, N,N-dimethylformamide (DMF) being so far the only compound studied.[22] Upon anodic oxidation in formic acid/sodium formate it gives a high yield (79 %) of N-formyloxymethyl-N-methylformamide.

An indirect mechanism involving formyloxy radical was originally postulated in view of the fact that formate ion is more easily oxidized than DMF, and we can see that this would result in a very facile H atom transfer process from the CH_2−H bond of DMF ($E_a = 2.2$ kcal mol^{-1}). The far lower yield of the corresponding acetoxylation process (7 %) would then be explicable by competition from the much higher rate of decarboxylation of the acetoxy

radical (Table 1). This reasoning implies that a free, not adsorbed and hence more stable, radical is the attacking species (for a detailed discussion, see below).

Anodic acetoxylation. In homogeneous solution, acetoxy radical is a very unstable species with a rate constant for decarboxylation of *ca.* 4×10^8 s^{-1} at 20 °C ($E_a \sim 7$ kcal mol^{-1}). It therefore is expected to abstract H atoms under very favourable conditions only, *e.g.*, in reactions with $E_a \leq 4$ kcal mol^{-1}.

It is generally assumed among physical electrochemists that acetoxy radical is formed by discharge of adsorbed acetate ion at the platinum anode,[23] and that it is adsorbed to the surface. Recently a variable frequency AC electrolytic technique (in essence, determination of the lowest frequency of the AC current at which gas evolution and hence the Kolbe reaction ceases) was used to estimate the heat of adsorption of acetoxy radical at the Pt anode, and the corresponding half-life of the adsorbed radicals (Table 1). As seen from the data given, adsorption of AcO⋅ on Pt from CH_3COOH causes an increase in stability by a factor of *ca.* 10^7. It should be noted that this result depends critically on the assumption that the decarboxylation step − and not the electron transfer step − is the rate-determining one.

What are then the implications for the anodic acetoxylation reaction of an enhanced stability of AcO⋅ by adsorption as compared to its solution properties? Table 2 shows that AcO⋅ in solution ought to react with H atom abstraction from compounds containing allylic and benzylic C−H bonds, and of course also $CONCH_2$−H bonds, but what do we expect from an adsorbed AcO⋅? If the same decrease in reactivity *vs.* C−H bonds as in decarboxylation is noted, we would reach E_a values in excess of 12 kcal mol^{-1} even for the most reactive C−H bonds, and hence have a system with two relatively slow competing reactions. If *no* decrease in reactivity *vs.* C−H bonds takes place, a vastly enhanced proportion of product(s) would be formed *via* AcO⋅ (of course the same argument holds for other reaction modes of AcO⋅, for example, addition to double bonds or systems of double bonds) since decarboxylation is so strongly suppressed. In combination with the assumption [7] that adsorbed AcO⋅ might well be formed at potentials considerably lower than that required for the Kolbe reaction proper, we have a series of seemingly strong arguments in favor of AcO⋅ mediated anodic acetoxylation mechanisms. The previously noted higher

efficiency of anodic formyloxylation of DMF over acetoxylation would seem to point in the same direction.

Summarizing, we have three extreme cases of AcO$\cdot$ behaviour at a Pt anode, *viz.*

(1) same reactivity as in solution in all respects (*i.e.* the radical does not react until it is desorbed);

(2) strongly reduced reactivity in all respects (*i.e.* the radical reacts in the adsorbed state);

(3) strongly reduced reactivity with respect to decarboxylation but with essentially unchanged reactivity toward C−H and C=C bonds (reaction still takes place in the adsorbed state).

Case 3 can be easily dismissed on the basis of the simple experimental fact that current yields of acetoxylation products in HOAc/OAc⁻ from toluene[24] (calculated $E_a = 3.4$ kcal mol⁻¹), cyclohexene[25] (calculated $E_a < 2.9$ kcal mol⁻¹) and DMF[22] (calculated $E_a = 1.9$ kcal mol⁻¹) are very low, 2, 8, and 7 %, respectively. In general, a number of substrates with high oxidation potentials give low yields of acetoxylation products in KOAc/OAc⁻ in spite of the fact that a case 3 acetoxy radical would at least abstract hydrogen atoms from them with great ease. Neopentylbenzene is an extreme case;[26] no α acetoxylation occurs in HOAc/AcO⁻, whereas in HOAc/BF₄⁻ it does take place, the *direct* mechanism (RH → RH$\cdot^+$ → R$\cdot$ + H⁺) now being in effect. Clearly, an acetoxy radical with unaltered reactivity *vs.* C−H bonds and an E_a for decarboxylation >16 kcal mol⁻¹ would display a lot more acetoxy radical chemistry with these substrates present. No such indications are discernible.

Case 2 is a more difficult one. The case 2 acetoxy radical is now of the same or lower reactivity as benzoyloxy (see Table 1), and a great deal of evidence, discussed earlier[5,6] (see also below), can be brought forward to show that anodically generated benzoyloxy radical indeed is responsible for much of the chemistry observed during anodic oxidation of PhCOO⁻/substrate systems. A comparison of isomer distributions from the anodic and diacyl peroxide/Cu(II) induced aromatic acyloxylations[6] showed that the similarities between the heterogeneous and homogeneous reactions indeed are profound.
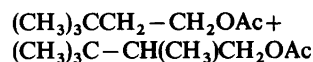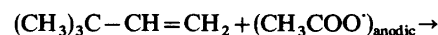
The close analogy between anodic and diacyl peroxide/Cu(II) induced acyloxylation is one of the strongest arguments in favor of the adsorbed acetoxy radical mechanism (provided we accept that the latter process does proceed *via* an initial acyloxy radical attack, and most evidence is in favor of this

assumption). Until now, no unambiguous critical experiments have been designed to decide directly for or against the adsorbed acetoxy radical mechanism, and it might be impossible even in principle.

The case 1 acetoxy radical, as generated in homogeneous solution by thermal decomposition of diacetyl peroxide, is a very unstable species which decarboxylates extremely rapidly and has little chance to enter into other modes of reaction, except possibly for cage reactions. It is this extreme instability that among other things led to the suggestion and predominance of direct anodic acetoxylation mechanisms

$$(i.e. \text{ R-H} \overset{-e}{\rightarrow} \text{RH}\cdot^+ \xrightarrow{\text{OAc}^-} \dot{\text{R}}\text{(H)OAc}\,;$$
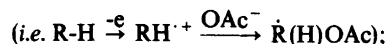
in fact we are fifteen years later aware of only one anodic acetoxylation reaction that cannot be easily explained on the basis of a direct mechanism (eqn. 4), namely the formal addition of CH₃COO−H and CH₃COO−CH₃

$$(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2+(\text{CH}_3\text{COO}\cdot)_{\text{anodic}} \rightarrow$$

$$(\text{CH}_3)_3\text{C}\dot{\text{C}}\text{H}-\text{CH}_2\text{OAc}\xrightarrow[\text{CH}_3\text{ (from CH}_3\text{COO}\cdot)]{\text{H}\cdot\text{ (from C}-\text{H)}} \quad (4)$$

$$(\text{CH}_3)_3\text{CCH}_2-\text{CH}_2\text{OAc}+$$
$$(\text{CH}_3)_3\text{C}-\text{CH(CH}_3)\text{CH}_2\text{OAc}$$

across the double bond of 3,3-dimethyl-1-butene.[27] This substrate is highly resistant toward oxidation and acetoxy radical attack is in principle possible, and in fact the only feasible way to explain the formation of the products of eqn. 4.

As seen from Table 2 (reactions 11−13) a case 1 acetoxy radical is expected to abstract a hydrogen atom from activated positions like those in propene, toluene and DMF. We are convinced that such reactions take place − in parallel with the direct mechanism − in anodic oxidations of these and analogous substrates in the presence of AcO⁻, but cannot at present suggest any experiments to distinguish between these possibilities. The possibility that CH₃ from decarboxylation of CH₃COO$\cdot$ is wholly or partly responsible for H atom abstraction also exists, and this particular problem can be solved experimentally (see below).

Benzoyloxylation. We have already discussed anodic benzoyloxylation in a different context[5,6] and concluded that this reaction in all probability is mediated by PhCOO$\cdot$. From the calculated E_a

values of Table 2 (especially reactions 16−19) one can see that H atom abstraction by PhCOO˙ should be a feasible process in competition with decarboxylation (Table 1, $E_a = 11 - 18$ kcal mol^{-1}). This of course applies to homogeneous reactions too.

Hydroxylation. The anodic hydroxylation of organic compounds has almost invariably been performed in acidic media, and it is therefore difficult to discuss this reaction type. If formed anodically, HO˙ would be expected primarily to attack C=C bonds or bond systems − as it does in homogeneous medium − but with suitable substrates H atom abstraction should be a very fast process.

In a few cases of electrolysis in hydroxide containing electrolytes (anodic oxidation of indan, tetralin and 6-methoxytetralin in t-BuOH−H$_2$O/NaOH) was exclusive α substitution actually observed.[28]

Methoxylation. Anodic methoxylation under conditions favoring the generation of methoxy radicals, i.e. in CH$_3$OH/CH$_3$O$^-$, has been little studied,[29] no doubt due to the extreme complexity of the reaction in cases where the substrate structure does not allow for specific pathways to be favored. Such cases are, for example, additions of the elements of CH$_3$O−OCH$_3$ to methoxyaromatics in CH$_3$OH/CH$_3$ONa to give quinone ketals.[30]

For simple alkylaromatics methoxylation in the CH$_3$OH/CH$_3$ONa gives complex mixtures with α-methoxylated products as the only isolated products. The low current efficiencies (in the range of 3−15 %) for formation of α methoxy and other products and the complexity of the product mixture speak strongly for a mechanism involving initial formation of methoxy radical by one-electron transfer from methoxide ion. Table 2 (reactions 27−34) show calculated E_a values for H atom abstraction by methoxy radical very well in agreement with this postulate.

Amines are easily oxidized substrates, and hence the direct-mechanism has been favored even in systems where methoxy radical might be formed (MeOH/MeO$^-$).[31] In view of the very low calculated E_a value for hydrogen atom abstraction (Table 2, reaction 32) from trimethylamine by methoxy radical, this reaction should be subjected to further critical studies (compare also the discussion on the α methoxylation of aliphatic and alicyclic ethers;[32] reaction 31 in Table 2).

Nitrooxylation. The anodic oxidation of organic substrates with a nitrate salt as the supporting electrolyte often results in higher current efficiencies than when a salt of the solvent ion is used (e.g. NO$_3^-$ vs. CH$_3$O$^-$ in CH$_3$OH and vs. CH$_3$COO$^-$ in CH$_3$COOH).[2] The problem of deciding the type of mechanism has been especially pronounced for the anodic oxidation of alkylaromatics in AcOH/NO$_3^-$, since oxidation potentials for substrate and nitrate ion are too close for CPE to be a useful diagnostic.[33] We recently showed[10] that NO$_3^-$ should abstract H˙ from many types of C−H bonds with ease (as also experiments indicate) and therefore concluded that indirect mechanisms might operate in many such anodic reactions. Table 2 contains additional E_a values for nitrate radical reactions. An interesting experimental test would be to oxidize an aldehyde (reactions 42 and 45) in the presence of nitrate ion (CPE at its oxidation potential), and look for the formation of an acyl nitrate. Since the aldehyde should be very resistant toward ET oxidation, the formation of an acyl nitrate should corroborate the indirect mechanism (cf. also below the anodic generation of RCOCH$_3$ from RCHO under Kolbe conditions).

Cyanation. This reaction continues to be the mechanistically most puzzling one among the anodic processes, and the calculations performed here do not resolve the difficulties; in view of the unusually large differences between calculated E_a values for hydrogen atom abstraction by CN˙ − in either mode of attack − and experimental values, one might say that a further dimension of complexity has been added. We will either have to say that the BEBO method fails completely for cyano radical hydrogen abstraction reactions − as for chlorine atom reactions − or that reported rate constants for such processes, in fact, pertain to other types of reactions. The latter strategy would obviously be the more attractive one, since one of the most intriguing and puzzling features of anodic cyanation is that it does not take place in the α position of alkylaromatics − and that is the essential result of the E_a calculations of Table 2. On the other hand it is not easy to suggest other reaction modes in simple systems like CN˙/CH$_4$. We can only note the apparent discrepancy already mentioned above (the relatively large difference in E_a for CN˙+CH$_4$ as estimated by different methods), and hope for a stronger interest in determining the earthly proper- of this interesting radical; most reports concern its presence and properties in heavenly objects like stars and galaxes! As for anodic cyanation, the situation is, in our opinion, still best summarized

as in Ref. 6.

Methylation. Anodic methylation is a well-known and amply documented side-reaction during acetoxylation, and there is general agreement that this reaction type is due to methyl radicals formed by decarboxylation of acetoxy radical.[2] The reaction has been extended to other radicals, like higher alkyl and CF_3, with moderate success; yields are unfortunately low and far from those obtained in the Minisci reaction, in which alkyl radicals are formed in homogeneous medium by $S_2O_8^{2-}$ induced decarboxylation of carboxylate ions.[34a]

As for the problem at hand, to assess the possibility of hydrogen atom abstraction by anodically generated methyl radical, it is not possible to directly distinguish between that and abstraction by acetoxy radical, since the latter is estimated to be a considerably faster process (see Table 2). In order to make such a distinction an analysis of the anode gases must show that the amount of products of suspected methyl radical origin is equal to or less (remember the possibility of a *direct* mechanism) than the amount of methane formed. Even so, one cannot be completely sure; for absolute certainty a suitably deuterated substrate must be used and the formation of matching amounts of correctly labelled methane and radical abstraction derived products must be established. The closest one can get to such a rigorous experiment is due to Clusius who electrolyzed CD_3COO^- in water and obtained a small amount of CD_4, consistent with attack of CD_3 upon a $C-D$ bond.[34b]

The last-mentioned result shows that reaction 68, with an experimental E_a of 10.2 kcal mol^{-1}, can take place under Kolbe conditions and it is therefore possible that methyl radical abstraction can occur for other substrates with lower E_a's as well. An interesting case is acetaldehyde, predicted to react with CH_3 at the $C(O)-H$ bond (reaction 67; compare with reaction 68). Experiments show that this reaction takes place at the formyl hydrogen in heptanal[35] and benzaldehyde.[36] Since aldehydes are estimated to have very high oxidation potentials — certainly above that required for acetate ion oxidation — it is highly probable that the reaction is initiated by radical attack (CH_3 or CH_3COO) upon the formyl hydrogen.

Methoxycarbonylation. The methoxycarbonyl radical can be generated by one-electron oxidation of methyl potassium oxalate (eqn. 5) and is known to add readily to added olefins or polyenes.[2]
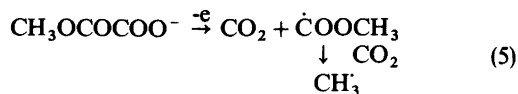
$$CH_3OCOCOO^- \xrightarrow{-e} CO_2 + \dot{C}OOCH_3$$
$$\downarrow \quad CO_2 \qquad (5)$$
$$CH_3$$

Table 1 shows that methoxycarbonyl is more stable toward decarboxylation than acetoxy by a factor of 10^2-10^3. Homogeneously generated methoxycarbonyl attacks benzene derivatives in the nucleus to give substituted methyl benzoates in preference to decarboxylation.[37] With toluene in excess bibenzyl was, however, the main product, indicating that either methoxycarbonyl or methyl radical readily abstracts hydrogen from the benzylic position.

Reaction 75 in Table 2, attack of methoxycarbonyl upon toluene, has a calculated E_a of 9.1 kcal mol^{-1}, well in the range for a relatively efficient reaction to occur. In combination with the fact that methoxycarbonyl is known to attack aromatics in the nucleus (see above), one would expect that anodic aromatic methoxycarbonylation should be a reaction of wide scope provided the electrochemical characteristics of eqn. 8 are the correct ones (relatively low oxidation potential of $^-OOCCOOCH_3$, very high decarboxylation rate of the corresponding radical).

Azidation. The azide radical can be generated by anodic oxidation of azide ion in acetic acid.[38] It adds readily to double bonds of added substrates

1
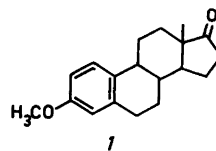
to give diazides but also substitutes hydrogen in suitably substituted compounds, *e.g.* alkenes, to give alkenyl azides. The latter process is calculated to have an E_a of 11 kcal mol^{-1} (Table 2, reaction 82). The only benzylic azidation reaction reported so far appears to be for 3-methoxyestra$-1,3,5(10)$-trienes (*1*), and it remains to evaluate the full scope of this reaction. Most likely, it proceeds *via* an indirect mechanism (see Table 2, reaction 81).

Possible role of perchlorate radical in anodic processes. Perchlorate ion is oxidized above *ca.* 2.5 V to give chlorine dioxide and oxygen,[40] presumably *via* perchlorate radical (eqn. 6) and this

$$ClO_4^- \rightarrow ClO_4 \rightarrow ClO_2 + O_2 \qquad (6)$$
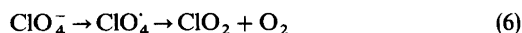
radical has often been implicated as initiator of anodic processes. With the paucity of data per-

Table 3. Input data for the calculations given in Table 2 (those not given were taken from Ref. 15). Unless otherwise stated, D_o values were calculated from data given in Refs. 44, 45 and 46. r_e values were taken from Ref. 47 and ω_o values were taken from Ref. 68.

Molecule and bond	$D_o/$ kcal mol^{-1}	$r_e/$Å	$\omega_o/$cm^{-1}	Remarks
HCOO – H	106.6	0.984	3550	
HCOO – CH$_3$	83.4	1.43	913	ω_o, Ref. 48[a]
HCOO – C$_2$H$_5$	83.7	1.43	913	[b]
HCOO – CHMe$_2$	83.0	1.43	913	[b]
HCOO – CMe$_3$	83.0	1.43	913	[b]
HCOO – CH$_2$Ph	70.6	1.43	813	[c]
HCOO – CH$_2$(CH$_3$)NCHO	72	1.43	913	[b]
HCON(CH$_3$)CH$_2$ – H	85	1.08	2940	D_o, see text
CH$_3$COO – H	112	0.984	3550	D_o, Ref. 50
CH$_3$COO – CH$_3$	86.4	1.43	960	[d]
CH$_3$COO – C$_2$H$_5$	86.7	1.43	960	[d]
CH$_3$COO – CHMe$_2$	86.0	1.43	960	[d]
CH$_3$COO – CMe$_3$	86.0	1.43	960	[d]
CH$_3$COO – allyl	77.5	1.43	960	[d]
CH$_3$COO – CH$_2$Ph	73.6	1.43	860	ω_o, see [c]
CH$_3$COO – CH$_2$(CH$_3$)NCHO	75	1.46	1000	D_o, see text: ω_o, estimated
PhCOO – H	102	0.984	3550	D_o, Ref. 53
PhCOO – CH$_3$	82.4	1.43	979	D_o, Ref. 45: ω_o, weighted value, Ref. 54
PhCOO – C$_2$H$_5$	82.7	1.43	979	[e,f]
PhCOO – CHMe$_2$	82.0	1.43	979	[e,f]
PhCOO – CMe$_3$	82.0	1.43	979	[e,f]
PhCOO – CH$_2$Ph	69.6	1.43	879	[e] ω_o, see [c]
PhCOO – CH$_2$(CH$_3$)NCHO	71.0	1.43	1000	[e] ω_o, estimated
HO – CH$_2$Ph	78.4	1.43	1010	ω_o, Ref. 55
HO – CH$_2$(CH$_3$)NCHO	75	1.43	1000	ω_o, estimated
MeO – CH$_2$Ph	74	1.43	941	[g]
MeO – CH$_2$OCH$_3$	83.9	1.382	1117	r_e, Ref. 56: ω_o, Ref. 57
MeO – CH$_2$NMe$_2$	83.9	1.382	1117	[h]
MeO – CH$_2$(CH$_3$)NCHO	75	1.46	1000	D_o, see text: ω_o, estimated
MeO – CONMe$_2$	99.6	1.33	1116	[i]
Me$_2$NCO – H	95.3	1.085	2928	[j], r_e and ω_o, Ref. 59
Me$_2$NCH$_2$ – H	86.6	1.112	2799	Ref. 60
·NO$_2$O – CH$_3$	80.6	1.437	1005	r_e, Ref. 61: ω_o, Ref. 62
NO$_2$O – C$_2$H$_5$	80.0	1.437	1005	[k]
NO$_2$O – CHMe$_2$	80.0	1.437	1005	[k]
NO$_2$O – C$_6$H$_{11}$	80.1	1.437	1005	[k]
NO$_2$O – allyl	67.5	1.437	1005	Ref. 10
NO$_2$O – CH$_2$Ph	67.5	1.437	900	D_o and r_e, Ref. 10: ω_o, see [c]
NO$_2$O – CH$_2$OCH$_3$	80	1.437	1005	[k,l]
NO$_2$O – COCH$_3$	97	1.37	1200	Ref. 10
NO$_2$O – CH$_2$CHO	76	1.437	1005	Ref. 10
NO$_2$O – CH$_2$COOH	76	1.437	1005	Ref. 10
NO$_2$O – CH$_2$OH	80	1.437	1005	Ref. 10
NO$_2$O – CH$_2$CN	80	1.437	1005	[k,l]
NO$_2$O – CH$_2$(CH$_3$)NCHO	75	1.437	1005	D_o, see text: [k]

$ClO_3O-C_2H_5{}^m$	80.1	1.437	1005	
$ClO_3O-C_6H_{11}{}^m$	80.1	1.437	1005	
$ClO_3O-CH_2Ph^m$	67.5	1.437	900	
$ClO_3O-CH_2CN^m$	80	1.437	1005	
$ClO_3O-CH_2(CH_3)NCHO^m$	75	1.437	1005	
$NC-CH_3$	119.9	1.458	920	^{n}: r_e and ω_o, Ref. 63
$NC-C_2H_5$	115.5	1.458	820	^{n,o}: ω_o, Ref. 64
$NC-CHMe_2$	114	1.458	820	^{n,o}: ω_o, Ref. 64
$NC-CMe_3$	112.7	1.458	820	^{n,o}: ω_o, Ref. 64
$NC-CH_2Ph$	101.5	1.458	720	^{n,o}: ω_o. see ^{c}
$NC-CH_2NMe_2$	100	1.458	820	^{n,o}: ω_o. Ref. 64
CH_3-CH_2CHO	85.5	1.541	997	^{p}
CH_3-CH_2COOH	85	1.54	995	^{q}
CH_3-CH_2CN	81	1.54	965	^{r}
$CH_3-CH_2(CH_3)NCHO$	85	1.54	950	D_o, see text; ω_o, estimated
$CH_3-CONMe_2$	92	1.52	1000	^{s}; ω_o, estimated
$CH_3-COOCH_3$	92.0	1.52	844	ω_o, see ^{t}
$PhCH_2-COOCH_3$	75.0	1.52	844	D_o, estimated: r_e and ω_o, see ^{s}
N_3-CH_3	81.1	1.468	910	D_o. see ^{t}: r_e. Ref. 65: ω_o, Ref. 66
$N_3-C_2H_5$	81.1	1.468	910	
N_3-CHMe_2	81.1	1.468	910	D_o, see ^{t}: r_e and ω_o, see ^{u}
N_3-CMe_3	81.1	1.468	910	
$N_3-C_6H_{11}$	81.1	1.468	910	
N_3-CH_2Ph	69.0	1.468	810	^{v}; r_e, see ^{u}; ω_o, see ^{c}
N_3-allyl	69.0	1.468	910	^{x}; r_e and ω_o, see ^{u}

^{a} Ref. 49 gives 925 cm^{-1} which gives essentially unchanged E_a values. ^{b} D_o taken to be 3 kcal lower than for the corresponding acetate, as is the case for methyl formate; ω_o assumed to be the same as for methyl formate. ^{c} D_o taken to be 3 kcal lower than for the corresponding acetate, as is the case for methyl formate, ω_o taken to be 100 cm^{-1} lower than ω_o for the corresponding methyl or ethyl ester (see Ref. 10). ^{d} The ω_o value was adopted from data in Ref. 48. With $\omega_o = 842$ cm^{-1} (Ref. 51) E_a values become 1.3 – 2.1 kcal larger, whereas with $\omega_o = 1060$ cm^{-1} (Ref. 48) they are 0.8 – 1.2 kcal lower. ^{e} D_o taken to be 4 kcal lower than D_o for the corresponding acetate, as is the case for methyl benzoate. ^{f} ω_o taken to be the same as for methyl benzoate. ^{g} ω_o assumed to be the same as for the corresponding t-BuO compounds (Ref. 15). ^{h} Assumed to be the same as for dimethoxymethane. ^{i} D_o estimated value for dimethyl carbonate, starting from ΔH_f° for diethyl carbonate (Ref. 45); r_e and ω_o assumed to be the same as in dimethyl carbonate (Ref. 58). ^{j} D_o assumed to be the same as for methyl formate (Ref. 46). ^{k} r_e and ω_o same as for methyl nitrate. ^{l} D_o assumed to be the same as for ethyl nitrate. ^{m} Since no experimental data are available, values for perchlorate esters were assumed to be the same as for the corresponding nitrates. ^{n} D_o calculated using $\Delta H_f^\circ(CN\cdot) = 101$ kcal mol^{-1} (Ref. 44). ^{o} r_e assumed to be the same as in acetonitrile. ^{p} Assumed to be the same as for acetone. ^{q} Assumed to be approximately the same as for acetone. ^{r} Assumed to be the same as in propane. ^{s} Taken to be the same as for methyl acetate. ^{t} Calculated from ΔH_f° for azidocyclohexane and assumed to be the same for all alkyl azides involved. ^{u} Assumed to be the same as in methyl azide. ^{v} Estimated value. A far lower value, 50.5 kcal mol^{-1} was given in Ref. 67. This value leads to unrealistically low E_a values. ^{x} D_o assumed to be the same as for benzyl azide.

taining to the perchlorate radical reactions (reactions 48 – 52 of Table 2) in mind, it is obvious that H abstraction by $ClO_4^\cdot$ is a feasible process even for non-activated $C-H$ bonds (*e.g.*, reaction 49, Table 2). Whether this process actually takes place is open to discussion, however. Miller and co-workers[41] have shown that aliphatic esters and nitriles are substituted at non-activated $C-H$ bonds upon anodic oxidation in acetonitrile/Et_4NBF_4 in the presence of chloride ion, ClO_2 or ClO_4^-. The preparative results in all systems were closely similar, and it was concluded that an unknown radical, formed from the solvent-electrolyte system, attacks the aliphatic substrate with hydrogen atom abstraction. This temporarily removes perchlorate radical from the scene but of course then poses the problem of defining the unknown species.

DATA AND CALCULATIONS

The required input data for the BEBO and equibonding method are bond dissociation energies (D_o), bond length (r_e) and stretching frequencies (ω_o) for $R-H$, $X-H$ and $R-X$ (see eqn. 3). A large amount of such data was collected by Zavitsas[15] and these have been used here in the appropriate cases. The remaining data were either available through the literature or estimated by analogy with related structures (see Table 3).

For DMF, no D_o value for the NCH_2-H bond was to be found in the literature. It was, however, known[42] that hydroxyl radical abstracts a hydrogen atom from the $N-CH_3$ group of DMF with a rate constant of 1.7×10^9 M^{-1} s^{-1} at 25 °C. Using a value of log A of 10.0, E_a is then calculated to be 1.1 kcal mol^{-1}. By carrying through BEBO calculations with different pairs of NCH_2-H and NCH_2-OH bond dissociation energies, differing by 10 kcal mol^{-1}, it was found that D_o values of 85 and 75 kcal mol^{-1}, respectively, best reproduce the experimental E_a value (see Table 2).

For reactions involving perchlorate radical, data for the $R-O$ bond of perchlorate esters are understandably not available and therefore had to be estimated.

Calculations were performed using the BEBO method as originally described by Johnston[16] and modified by Gilliom,[17] and the equibonding method as described by Zavitsas.[15] A minor change was made in that D_e was used instead of D_o in computing the spectroscopic constant β; D_e is the correct parameter here according to standard textbooks.[43] From a practical point of view this change has no consequences (at most $0.1-0.2$ kcal mol^{-1} in E_a).

REFERENCES

1. Eberson, L. and Nyberg, K. *Adv. Phys. Org. Chem. 12* (1976) 1.
2. Ross, S. D., Finkelstein, M. and Rudd, E. J. *Anodic Oxidation*, Academic, New York 1975.
3. Bard, A. J., Ledwith, A. and Shine, H. J. *Adv. Phys. Org. Chem. 13* (1976) 156.
4. Eberson, L., Blum, Z., Helgée, B. and Nyberg, K. *Tetrahedron 33* (1977) 731.
5. Eberson, L. and Nyberg, K. *Acta Chem. Scand. B 32* (1978) 235.
6. Eberson, L. and Nyberg, K. *Acta Chem. Scand. B 32* (1978) 520.
7. Mirkind, L. A. *Russ. Chem. Rev. 44* (1975) 999.
8. Rozhkov, I. N. *Russ. Chem. Rev. 45* (1976) 615.
9. Schmidt, W. and Steckhan, E. *J. Electroanal. Chem. 89* (1978) 215.
10. Eberson, L. and Oberrauch, E. *Acta Chem. Scand. B 33* (1979) 343.
11. Gilbert, B. C., Holmes, R. G. G., Marshall, D. R. and Norman, R. O. C. *J. Chem. Research* (1977) 172.
12. Shreider, V. A. and Rozhkov, I. N. *Bull. Acad. Sci. USSR 231* (1976) 1269.
13. Schwerzel, R. E., Lawler, R. G. and Evans, G. T. *Chem. Phys. Lett. 29* (1974) 106.
14. Samskog, P. O., Nilsson, G. and Lund, A. *J. Chem. Phys. 68* (1978) 4986.
15. Zavitsas, A. A. and Melikian, A. A. *J. Am. Chem. Soc. 97* (1975) 2757.
16. Johnston, H. S. and Parr, C. *J. Am. Chem. Soc. 85* (1963) 2544.
17. Gilliom, R. D. *J. Am. Chem. Soc. 99* (1977) 8399.
18. Müller, E. and Huber, H. *Chem. Ber. 96* (1963) 670.
19. Boden, J. C. and Thrush, B. A. *Proc. R. Soc. London A 305* (1968) 107.
20. Bullock, G. E. and Cooper, R. *J. Chem. Soc. Faraday Trans. 1 68* (1972) 2185.
21. Trotman-Dickenson, X. and Milne, G. S. *Tables of Bimolecular Gas Reaction* NSRDS-NBS 9, National Bureau of Standards, Washington, D.C. 1967.
22. Ross, S. D., Finkelstein, M. and Petersen, R. C. *J. Org. Chem. 31* (1966) 128.
23. Vijh, A. K. and Conway, B. E. *Chem. Rev. 67* (1967) 623.
24. Ross, S. D., Finkelstein, M. and Petersen, R. C. *J. Org. Chem. 35* (1970) 781.
25. Shono, T. and Ikeda, A. *J. Am. Chem. Soc. 94* (1972) 7892.
26. Sternerup, H. *Acta Chem. Scand. B 28* (1974) 969.
27. Smith, W. B. and Yuh, Y. H. *Tetrahedron 24* (1968) 1163.
28. Juday, R. E. *J. Org. Chem. 22* (1957) 532.
29. For a summary, see Weinberg, N. L. In (Weinberg, N. L., Ed.,) *Technique of Electroorganic Synthesis*, Part I, Wiley, New York 1974, Chapter 4.
30. Henton, D. R., Chenard, B. L. and Swenton, J. S. *Chem. Commun.* (1979) 326; Dolson, M. G., Jackson, D. K. and Swenton, J. S. *Chem. Commun* (1979) 327 and references therein.
31. Barry, J. E., Finkelstein, M., Mayeda, E. A. and Ross, S. D. *J. Org. Chem. 39* (1974) 2695.
32. Shono, T. and Matsumara, Y. *J. Am. Chem. Soc. 91* (1969) 2803; Scheeren, J. W., Goossens,

H. J. M. and Top, A. W. H. *Synthesis* (1978) 283.

33. Nyberg, K. *Acta Chem. Scand. 24* (1970) 473: *25* (1971) 3246.

34. a. Minisci, F. *Synthesis* (1973) 1: b. Clusius, K. and Schanzer, W. *Z. Phys. Chem. Abt. A 192* (1943) 273.

35. Takeda, A., Wada, S., Torii, S. and Matsui, Y. *Bull. Chem. Soc. Jpn. 42* (1969) 1047.

36. Takeda, A., Torii, S. and Oka, H. *Tetrahedron Lett.* (1968) 1781.

37. Fiorentino, M., Testaferri, L., Tiecco, M. and Troisi, L. *J. Org. Chem. 41* (1976) 173.

38. Schäfer, H. J. *Chem. Ing. Tech. 42* (1970) 164.

39. Ponsold, K. and Kasch, H. *Tetrahedron Lett.* (1979) 4463.

40. Cauquis, G. and Serve, D. *J. Electroanal. Chem. 27* (1970) App. 3 – 6.

41. Miller, L. L. *Pure Appl. Chem. 51* (1979) 2125: Miller, L. L. and Katz, M. *J. Electroanal. Chem. 72* (1976) 329; Miller, L. L. and Ramachandran, V. *J. Org. Chem. 39* (1974) 369.

42. Hayon, E., Ibata, T., Lichtin, N. N. and Simic, M. *J. Am. Chem. Soc. 92* (1970) 3898.

43. Moore, W. J. *Physical Chemistry*, 5th Ed., Longmans, London 1972, p. 769.

44. Benson, S. W. *Thermochemical Kinetics*, 2nd Ed., Wiley, New York 1976.

45. Pedley, J. B. and Rylance, J. *Sussex-NPL Computer Analyzed Thermochemical Data: Organic and Organic and Organometallic Compounds*, University of Sussex, Sussex 1977.

46. Egger, K. W. and Cocks, A. T. *Helv. Chim. Acta 56* (1973) 1516.

47. Sutton, L. E., Ed., *Interatomic Distances*, Special Publications Nos. 11 and 18, The Chemical Society, London 1958 and 1965.

48. Moravie, R. M. and Corset, J. *J. Mol. Struct. 30* (1976) 113.

49. Wilmshurst, J. K. *J. Mol. Spectrosc. 1* (1957) 201.

50. Kerr, J. A. *Chem. Rev. 66* (1966) 465.

51. George, W. O., Houston, T. E. and Harris, W. C. *Spectrochim. Acta 30 A* (1974) 1035.

52. Jaffe, L., Prosen, E. J. and Szwarc, M. *J. Chem. Phys. 27* (1957) 416.

53. Mortimer, G. T. *Reaction Heats and Bond Strengths*, Pergamon, Oxford 1962.

54. Boerio, F. J. and Bahl, S. K. *Spectrochim. Acta 32 A* (1976) 987.

55. Zeiss, H. H. and Tsutsui, M. *J. Am. Chem. Soc. 75* (1953) 897.

56. Astrup, E. E. *Acta Chem. Scand. 27* (1973) 3271.

57. Nukada, K. *Spectrochim. Acta 18* (1962) 745.

58. Collingwood, B., Lee, H. and Wilmshurst, J. K. *Aust. J. Chem. 19* (1966) 1637.

59. Kaufmann, G. and Leroy, M. J. F. *Bull. Soc. Chim. Fr.* (1967) 402.

60. McKean, D. C., Duncan, J. L. and Batt, L. *Spectrochim. Acta 29 A* (1973) 1037.

61. Cox, A. P. and Waring, S. *Trans. Faraday Soc. 67* (1971) 3441.

62. Lannon, J. A., Harris, L. E., Verderame, F. D., Thomas, W. G., Lucia, E. A. and Koniers, S. *J. Mol. Spectrosc. 50* (1964) 68.

63. Nagakawa, I. and Shimanouchi, T. *Spectrochim. Acta 18* (1962) 513.

64. Wurrey, C. J., Bucy, W. E. and Durig, J. R. *J. Phys. Chem. 80* (1976) 1129.

65. Anderson, D. W. W., Rankin, D. W. H. and Robertson, A. *J. Mol. Struct. 14* (1972) 385.

66. Thompson, W. T. and Fletcher, W. H. *Spectrochim. Acta 22* (1966) 1907.

67. Pepekin, V. I., Erlikh, R. D., Matyushin, Yu.N. and Lebedev, Yu.A. *Dokl. Phys. Chem. 214* (1974) 123.

68. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd Ed., Methuen, London 1966: *Advances in Infrared Group Frequencies*, Methuen, London 1968.