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Studies on Electrolytic Substitution Reactions. XIV. Comparison between Anodic and Cerium Ammonium Nitrate Oxidation of Isodurene in Acetic Acid

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Cerium ammonium nitrate oxidation of 1,2,3,5-tetramethylbenzene (isodurene) has been compared with its anodic oxidation in acetic acid/tetrabutylammonium nitrate. The reactions are very similar with respect to the composition of the mixture of isomeric acetates or nitrates formed, within each class of compound; the nitrate/acetate ratio is, however, considerably lower in the anodic experiments.

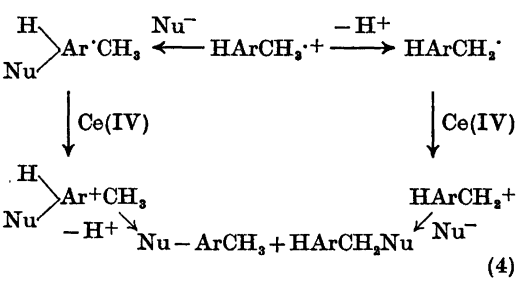
The mechanisms of these reactions are discussed with the usual dichotomy of electroorganic chemistry — direct or indirect mechanism? — as a starting point. It is concluded that anodic nitrooxylation and acetoxylation of isodurene in nitrate-containing electrolytes probably proceed *via* an indirect mechanism, and that cerium ammonium nitrate oxidation might occur *via* hydrogen atom transfer from the α carbon of the alkylaromatic compound to hexanitratocerate(IV) ion.

Cerium ammonium nitrate (CAN) has recently been used for effecting oxidative substitution of aromatics, *e.g.* nuclear acetoxylation of anisole [1] and mesitylene [2] and side-chain (α) acetoxylation/nitrooxylation of mesitylene,[2] isodurene,[2] 1,2,3-trimethylbenzene [2] and hexamethylbenzene [2] (eqns. 1 and 2). The mechanism was suggested [1–3] to involve initial one-electron transfer from substrate to Ce(IV), leading to a radical cation which in the appropriate case might either be attacked by the nucleophile at a ring position or lose a proton from the α position. A second electron transfer to Ce(IV) from the radical intermediate, followed by proton loss or capture by a nucleophile, respectively, completes the sequence (eqns. 3 and 4). An analogous mechanism was postulated for the oxidation of alkylaromatic hydrocarbons by cerium(IV) trifluoroacetate in trifluoroacetic acid.[4]

$$ArH + 2Ce(IV) + CH_3COOH \rightarrow ArOAc + 2Ce(III) + 2H^+ \quad (1)$$

$$ArCH_3 + 2Ce(IV) + CH_3COOH(NO_3^-) \rightarrow ArCH_2OAc(ArCH_2ONO_2) + 2Ce(III) + 2H^+(H^+) \quad (2)$$

$$HArCH_3 + Ce(IV) \rightleftharpoons HArCH_3^{\cdot +} + Ce(III) \quad (3)$$



(4)

The same mechanism is generally postulated for direct anodic substitution reactions and is denoted the ECEC mechanism [5] (E = electrochemical, C = chemical step). In view of our long-standing interest in comparing electrochemical and metal ion promoted oxidations,[6] we have extended our studies to CAN and anodic oxidation of a suitable substrate. In addition, the as yet unsettled problem of the

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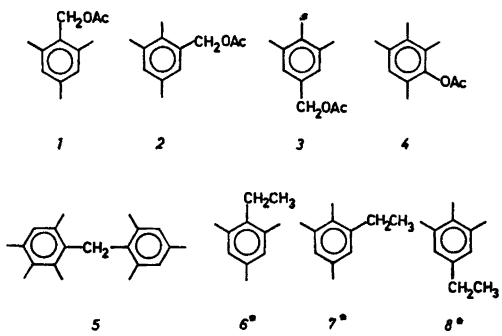
rôle of nitrate ion in anodic substitution [7–11] in electrolytes containing nitrate (direct or indirect mechanism?) might be further illuminated. Isodurene, 1,2,3,5-tetramethylbenzene, was chosen as the most suitable compound for this study, since CAN oxidation results of isodurene are available [2] and this hydrocarbon offers several possibilities of regioselectivity (side-chain *vs.* nuclear substitution, three side-chain positions).



* Only two of the three possible isomers in a 5:1 ratio were detectable.

RESULTS

1. *Electroanalytical study of isodurene.* As expected,[12] isodurene displayed irreversible electrochemical behavior upon cyclic voltammetry in HOAc/Bu_4NBF_4 (or KOAc or Bu_4NNO_3). A cyclic voltammogram at a sweep rate of 0.1 V s^{-1} in AcOH/0.1 M Bu_4NBF_4 shows four anodic waves (at 1.78, 1.99, 2.12 and 2.23 V *vs.* Ag/Ag^+ (0.1 M); all potentials given in the following are related to this reference electrode), the first of which is well-defined and the three others appear superimposed upon the rising wave with difficultly definable peak values. The peak current of the first wave, plotted *vs.* $(\text{sweep rate})^{1/2}$, showed that the corresponding oxidation process is irreversible. Under identical conditions 2,4,6-trimethylbenzyl acetate (*1*), the main product in the preparative electrochemical experiments, showed a peak potential of 2.08 V.

A similar study was performed in CH_3CN-HOAc(3:1)/Bu_4NBF_4 (0.1 M) with identical results. Since this medium exhibits a low background current, it could be used for constant current coulometry at the potential of the first wave, affording an *n* value of 1.97. No defined wave was seen in HOAc/KOAc due to the high background current whereas in HOAc/Bu_4NNO_3 a single wave at 1.82 V was observed.

2. *Preparative anodic oxidation of isodurene in acetic acid containing Bu_4NBF_4 or KOAc.* The compounds *1–8* were isolated or detected from preparative anodic oxidation of isodurene in acetic acid containing either an inert electrolyte (Bu_4NBF_4) or an acetate salt (KOAc; the results from anodic oxidation in nitrate electrolytes are reported below).

Table 1 summarizes preparative results (expts. 1–8) at different conversions and with different anode materials and supporting electrolytes. With an inert anion present, only side-chain acetoxylation (formation of *1–3*) is observed and in addition a relatively large proportion of the coupling product (*5*) is formed. With acetate ion present the proportion of *5* is smaller and the nuclear substitution product (*4*) is formed besides *1–3*. A slightly lower selectivity is indicated in the benzylic isomer ratios with acetate ion present. A comparison between platinum and graphite as anode material shows that graphite is the more favourable one; current yields are higher and the reaction is considerably more selective. In particular the yield of coupling product (*5*) and methylated products (*6–8*) is much lower.

3. *Preparative anodic oxidation of isodurene in acetic acid containing Bu_4NNO_3.* Using Bu_4NNO_3 (0.2 M) as the supporting electrolyte only side-chain substitution was observed. Both acetates (Table 1, experiment 9) and nitrates were formed, the nitrate/acetate (N/A) ratio being *ca* 0.25 (Table 2, expts. 11–13). At 10 % conversion the N/A ratio could only be obtained as the ratio between the 2,4,6-trimethylbenzyl derivatives, whereas at 90 % conversion the analytical method (NMR) also permitted an N/A ratio (0.28) for the 3,4,5-trimethylbenzyl derivatives to be estimated. This latter experiment was run at room temperature to avoid solvolysis of the nitrates.

4. *CAN oxidation of isodurene.* Results on this process are already available,[2] so we have here concentrated our efforts to CAN oxidations under conditions resembling the anodic reaction as closely as possible. Since it was found [2] that the N/A ratio in CAN oxidation was dependent

Table 1. Acetate isomer ratios in anodic and CAN oxidation of isodurene in acetic acid.

Exp. No.	Oxidant (electrode material)	Supporting electrolyte	Conversion/ F mol^{-1} or %	Composition of acetates: Benzylic [a] 1	2	3	Nuclear 4	Current yield/%	M/A [b]	C/A [c]
1	Anode(Pt) [d]	Bu_4NBF_4	0.2	75	4	21	0	17	0	0.40
2	Anode(Pt) [d]	Bu_4NBF_4	1.0	75	4	21	0	40	0	0.19
3	Anode(Pt) [d]	Bu_4NBF_4	1.8	75	4	21	0	67	0	0.12
4	Anode(C) [d]	Bu_4NBF_4	0.2	79	4	17	0	81	0	0.05
5	Anode(Pt) [d]	KOAc	0.2	68	6	26	18	24	0.7	0.03
6	Anode(Pt) [d]	KOAc	1.0	66	7	27	17	22	0.5	0.01
7	Anode(Pt) [d]	KOAc	1.8	66	8	26	17	20	0.4	0.01
8	Anode(C) [d]	KOAc	0.2	80	4	16	26	87	0.07	0.01
9	Anode(Pt) [e]	Bu_4NNO_3	0.2	77	7	16	0			
10	CAN[e,f]	—	10 %	79	7	14	0			
	CAN [2]	—	0 %	77	14	9	0			

[a] Normalized to 100 % for cases where *4* is formed. [b] Ratio of methylated products to acetates: $(6+7+8)/(1+2+3+4)$. [c] Ratio of coupling product to acetates: $5/(1+2+3+4)$. [d] At room temperature. [e] For benzylic nitrates, see Table 2. [f] The product mixture was solvolyzed with NaOAc added before analysis.

Table 2. Side-chain nitrate/acetate ratios in anodic and CAN oxidation of alkylaromatic compounds in acetic acid.

Exp. No.	Compound	Oxidant (temperature/°C)	$[NO_3^-]$/M	Nitrate/acetate ratio	Ref.
	Toluene	Anodic(20)	0.77	0.7	11
	Mesitylene	Anodic(20)	0.4	1.0 – 0.8 [a]	7
	Mesitylene	Anodic(20)	1.25	1.0	9
	Mesitylene	CAN(50)	0.048 [b]	1.5 [c]	2
11	Isodurene	Anodic(56) [d]	0.25	0.27 [i]	This work
12	Isodurene	Anodic(20) [h]	0.25	0.25 [i] (0.28) [j]	This work
13	Isodurene	Anodic(20) [h]	0.25	0.20 [l]	This work
14	Isodurene	CAN(56)	*ca.* 0.05 [e]	1.0 [m]	This work
15	Isodurene	CAN(56)	*ca.* 0.05 [f]	0.74	This work
	Isodurene	CAN(50)	0.048 [g]	2.2 [c]	2
	1,2,3-Trimethylbenzene	CAN(50)	0.048 [g]	~5	2
	Hexamethylbenzene	CAN(50)	0.042	> 1.4	2

[a] Between 20 and 100 % conversion (calculated for 2 F mol^{-1}). [b] Homogeneous system, calculated on the basis of [CAN] being 8×10^{-3} M at saturation.[2] [c] Extrapolated to zero % conversion. [d] At 10 % conversion (calculated for 2 F mol^{-1}). [e] Heterogeneous system, excess CAN, *ca.* 10 % conversion. [f] Heterogeneous system, excess substrate, *ca.* 10 % conversion. [g] Heterogeneous system. [h] At 90 % conversion (calculated for 2 F mol^{-1}). [i] Based on the 2,4,6-trimethyl derivatives. [j] Based on the 3,4,5-trimethyl derivatives. [k] Divided cell, 20 % conversion (calculated for 2 F mol^{-1}). [l] The 2,4,6/2,3,5/3,4,5 nitrate isomer ratio was 69/7/24. [m] The 2,4,6/2,3,5/3,4,5 nitrate isomer ratio was 79/6/15.

upon the amount of solid CAN present, the ratio being higher with increasing amount of solid, we soon realized that it was not possible to obtain identical reaction conditions. We therefore resorted to run experiments (heterogeneous) at low conversion, either by using an excess of CAN and discontinuing the experiment at about 10 % reaction (after 30 min at 56 °C, expt 14) or a 10:1 excess of substrate over CAN and running the reaction to completion (expt 15). In both cases we obtained lower N/A ratios than those reported (1.0 and 0.74, respectively *vs.* 2.2) which might be partly due to the use of a higher temperature (56 *vs.* 50 °C) in our study.

DISCUSSION

The results obtained in the electrochemical study of isodurene in HOAc/Bu_4NBF_4 and HOAc/KOAc are in good qualitative agreement with results from the anodic oxidation of other alkylaromatic hydrocarbons.[12] The observation of several voltammetric waves is well-known, and the exclusive formation of side-chain products with an inert electrolyte (Bu_4NBF_4) present is expected,[10,13,14] as is the partial switch to formation of methylated products (*6* – *8*) and the nuclear product (*4*) with acetate ion present.[10,15] The formation of the coupling product, *5*, is predominant in the non-nucleophilic electrolyte, CH_2Cl_2/Bu_4NBF_4 and is gradually suppressed as the medium becomes more nucleophilic.[16] All these features are predictable from current theory of electroorganic chemistry [5] and attest to the relatively high reliability of the ideas in this area.

As we move on to the electrolysis results with a nitrate salt as the supporting electrolyte, the unsettled problems, however, immediately become apparent. According to the ECEC mechanism (eqns 3 and 4) a benzyl cation is formed *via* the radical cation, and we would then predict a *higher* selectivity for the stronger nucleophile (NO_3^- is stronger as a nucleophile than acetic acid) as the benzylic cation becomes more stable; the reverse is indicated by the anodic results of Table 2.

The second mechanism proposed for the anodic nitrate reaction [9–11,17] is an indirect one, starting with a one-electron oxidation of NO_3^- to give $NO_3^\cdot$ which then abstracts a hydrogen atom from the α position of $ArCH_3$ (eqns. 5 and 6). The benzyl radical would then undergo the same steps as those terminating the ECEC mechanism (eqn. 4) which obviously poses the same problem as that indicated above.

$$NO_3^- \rightarrow NO_3^\cdot + e \quad (5)$$

$$ArCH_3 + NO_3^\cdot \rightarrow ArCH_2^\cdot + HNO_3 \quad (6)$$

Earlier work on the anodic oxidation of aromatic hydrocarbons in acetic acid/nitrate electrolytes [7,8] did not give any definitive evidence for either of the two mechanisms shown in eqns. 3 – 4 and 5 – 6 (the direct *vs.* indirect one). The best conclusion was that both mechanisms operate simultaneously, at least for substrates (*e.g.*, mesitylene and durene) with oxidation potentials close to that of nitrate ion, since neither of the mechanisms could singly account for all known facts.

Studies [18–21] on the anodic oxidation of nitrate ion in organic media have shown that nitrate radical is indeed formed (eqn. 5) at potentials above 1.3 V, but that it undergoes very fast follow-up reactions. Nitrate radical can also be generated by photolytic methods [22,23] or by thermolysis of dinitrogen pentoxide [24,25] and rates of attack upon organic molecules have been measured: Acetic acid [22] $(4.6 \pm 0.4) \times 10^4$ (liquid phase), aliphatic alcohols [23] $(1-4) \times 10^6$ (liquid phase), propene [25] $(3.2 \pm 0.2) \times 10^6$ (gas phase) and acetaldehyde [24] $(7 \pm 2) \times 10^5$ (gas phase) M^{-1} s^{-1}, all measured around 20 °C. In all cases except propene the reaction type was assumed to be hydrogen abstraction, most probably from carbon. For propene (and other alkenes as well) the gas phase data indicated attack of nitrate ion at the double bond; [25] on the other hand anodic oxidation of propene in acetic acid/lithium nitrate gave allyl nitrate in the potential range where propene cannot be oxidized.[21] We therefore assume that nitrate radical attacks a C–H bond of the methyl group in the gas phase experiments too.

In order to illuminate the problem of nitrate radical reactivity *vs.* alkylaromatic hydrocarbons we have calculated theoretical values of the activation energies (E^*) for a number of hydrogen atom abstractions by nitrate radical and a few other radicals of interest in anodic chemistry, using one of the semiempirical methods developed by Zavitsas *et al.*[26,27] These are

based upon the use of Morse potentials of the participating bonds, X–H and H–Y in eqn. 7, and for X–Y. Since the first version [26] turned out to be less suitable for our systems due

$$X-H+Y^{\cdot}\rightleftharpoons[X\cdots H\cdots Y]^{\ddagger}\rightleftharpoons X^{\cdot}+H-Y \qquad (7)$$

to their high exothermicity (in such cases, E^* values tend to come out negative) we have adopted Zavitsas' second approach [27] (the equibonding method [28]). Both methods were shown [26–31] to give very good agreement between calculated and experimental activation energies. The required input data in these models are bond dissociation energies (D_0) for X–H, H–Y and X–Y, and the corresponding bond lengths (r_e) and IR stretching frequencies (ω_0).

Table 3 shows calculated and experimental values for a number of reactions, using input data from Zavitsas' papers or from sources quoted in Table 4. For systems with X= benzyl ω_0(X–Y) values are not available, except in a few cases. We then based our estimates on the fact that in known cases ω_0(X–Y) for X=benzyl are approximately 100 cm^{-1} lower than those of the corresponding methyl and ethyl systems.

In most cases, several sources of uncertainty affect both theoretical and experimental activation energies in Table 3. Thus E_a values were calculated from rate data on the assumption that the A factor is 10^{10} M^{-1} s^{-1} (reactions 1–5, 8) whereas it in known cases of gas phase hydrogen atom abstraction from toluene [47] can vary between 10^6 and 10^{10} M^{-1} s^{-1}. Hence E_a values represent maximum values for these reactions. The E^* values are sensitive toward variations in the input data, especially D_0(X–Y) and ω_0(X–Y) which unfortunately are also the variables for which experimental data are scarce or lacking. We have then had to use data from analogous cases. As an example of the variation of E^* with ω_0(X–Y), a range of ±40 cm^{-1} around 900 cm^{-1} for reaction 6 gives E^* with a variation of ±4 kJ mol^{-1}, and

Table 3. Calculated (E^*) and experimental (E_a) energies of activation for hydrogen atom abstraction reactions of nitrate radical and some other radicals of interest.

Reaction No.	Reaction	E^*/kJ mol^{-1}	E_a/kJ mol^{-1}
1	$CH_3CO-H+NO_3^{\cdot}$	13	24 [a]
2	$HCOCH_2-H+NO_3^{\cdot}$	30	24 [a]
3	$Allyl-H+NO_3^{\cdot}$	6	22 [a]
4	$HOCOCH_2-H+NO_3^{\cdot}$	33	32 [a]
5	$HOCH_2-H+NO_3^{\cdot}$	30	23 [a]
6	$PhCH_2-H+NO_3^{\cdot}$	16	–
7	$PhCH_2-H+CH_3COO^{\cdot}$	7	–
8	$PhCH_2-H+HO^{\cdot}$	8	8 [b]
9	$PhCH_2-H+CH_3O^{\cdot}$	20	–
10	$PhCH_2-H+t\text{-}BuO^{\cdot}$	18	18[c]; 23 [c]
11	$PhCH_2-H+CH_3^{\cdot}$	31	31[d]; 40 [e]
12	$PhCH_2-H+CN^{\cdot}$	47	–

[a] From rate data quoted in text with an assumed log A value of 10. [b] From $k=4\times10^8$ M^{-1} s^{-1} (Ref. 32) and an assumed log A value of 10. [c] Refs. 27 and 33, respectively. [d] Ref. 34.

Table 4. Input data for the calculations reported in Table 3 (those not given were taken from Refs. 26 and 27, unless otherwise stated; remaining bond dissociation energies were calculated from data in Ref. 36).

Molecule and bond	D_0/kJ mol^{-1}	r_e/Å	ω_0/cm^{-1}
CH_3CO-H	364 [a]	1.114 [b]	2800 [c]
$HCOCH_2-H$	411 [d]	1.091 [d]	2981 [e]
$HOCOCH_2-H$	418 [f]	1.09 [g]	2968 [h]
O_2NO-H	425	0.96 [i]	3550 [j]
CH_3COO-H	462 [k]	0.984 [l]	3550 [c]
$NC-H$	505	1.0657 [m]	3311 [c]
$PhCH_2-ONO_2$	282	1.437 [q]	900 [n]
$CH_3CO-ONO_2$	406 [o]	1.37 [o]	1200 [c,o]
$HCOCH_2-ONO_2$	318 [p]	1.437 [q]	1005 [q]
$HOCOCH_2-ONO_2$	318 [r]	1.437 [r]	1005 [r]
$Allyl-ONO_2$	282 [s]	1.437 [s]	1005 [q]
$HOCH_2-ONO_2$	335 [q]	1.437 [q]	1005 [q]
$PhCH_2-OCOCH_3$	308	1.43	1000 [t]
$PhCH_2-OH$	328	1.43	1000
$PhCH_2-OCH_3$	310	1.43	941 [u]
$PhCH_2-CN$	425	1.46 [v]	854 [v]

[a] Ref. 36. [b] Ref. 37 [c] Ref. 38. [d] Value for acetone.[27] [e] Ref. 38. [f] Estimated from the values of CH_3COCH_2-H (411) and $NCCH_2-H$ (400). [g] Standard value. [h] Ref. 38. [i] Ref. 39. [j] Ref. 40. [k] *Cf.* also Ref. 41. [l] Value for monomeric formic acid.[42] [m] Ref. 43. [n] Estimated from that of methyl nitrate,[44] 1005 cm^{-1} (see text). [o] Taken to be the same as in $CH_3CO-OCH_3$. [p] Estimated by comparison of a series of $PhCH_2-X$ and CH_3COCH_2-X values [27] (average Δ *ca.* 36 kJ mol^{-1}). [q] Same as in methyl nitrate.[45] [r] Same as for $HCOCH_2-ONO_2$. [s] Same as for benzyl nitrate. [t] Estimated from that of methyl acetate (1097.6 cm^{-1}; weighted average [46]) according to text. [u] Value for $PhCH_2-OBu^t$. [v] Value for $PhCH_2-CH_3$.

with $D_0(X-Y)$ a range of ± 20 kJ mol^{-1} around 282 kJ mol^{-1} gives E^* for the same process with a variation of ± 8 kJ mol^{-1}.

These sources of error notwithstanding, the E^* and E_a values of Table 3 show that nitrate radical attack upon C–H bonds is a very fast process. For toluene E^* is 16 kJ mol^{-1}, a value that we with reasonable certainty can assume to be close to the experimental one. A pertinent comparison is the allyl–H system (reaction 3), normally considered to be very similar to the benzyl–H system, where both E^* and E_a are ≤ 22 kJ mol^{-1}, indicating very high reactivity of nitrate radical.

A few other systems of interest in anodic chemistry are included. The acetoxy radical (reaction 7), albeit with an E_a for decarboxylation [5a,48] ($CH_3COO^{\cdot} \rightarrow CH_3^{\cdot} + CO_2$) of 28 kJ mol^{-1} is certainly reactive enough to abstract a hydrogen atom from toluene before it decarboxylates. The remaining oxygen-centered radicals of Table 3 (reactions 8–11) are known or predicted to react very rapidly with toluene, whereas cyano radical is predicted to react much slower (reaction 12). The implications of these and other results will be analyzed in a forthcoming publication. It only remains to reiterate our recent conclusion,[5a,49,50] that the problem of distinguishing direct and indirect mechanisms in anodic substitution is far from solved and needs a lot more thoughtful study.

Returning to our original problem, it is apparent that the indirect mechanism (eqns. 5 and 6) cannot be ruled out in the anodic substitution of isodurene in acetic acid/nitrate ion. The peak potential of isodurene is 1.82 V at which nitrate ion is also oxidized. Assuming that the indirect pathway is indeed the preferred one, the isomer distribution of the benzylic acetates (*1–3*) should be governed by the stability of the benzylic radicals formed – and this is actually observed [2,51] – whereas in the direct mechanism the distribution of positive charge in the radical cation is expected to have a predominant influence. It was shown by Nyberg [16] that the anodic dehydrodimerization of methylaromatic hydrocarbons in acetonitrile/Bu_4NBF_4 – which must take place *via* a radical cation mechanism – is directed toward the biaryl coupling mode (nuclear substitution) if the positive charge density is high in unsubstituted ring positions and the diphenylmethane coupling mode (side-chain substitution) when the positive charge density is high at the position(s) adjacent to a methyl group.

An INDO calculation [52] showed that isodurene has the following distribution of positive charge in the ring (expressed in % of positive charge at each ring carbon of the total charge at all six carbons): C-1 and C-3 16, C-2 31, C-4 and C-6 1, and C-5 35 %. Application of the rule above would give the order between *1*, *2* and *3* in a direct mechanism as *3* > *1* > 2, whereas in fact we observe *1* > *3* > *2*.

The above reasoning favors the indirect mechanism in the anodic substitution of isodurene with nitrate ion present (and, by analogy, also with acetate ion as nucleophile). In view of the empirical similarity of the anodic and CAN oxidation of isodurene, it is tempting to suggest an analogous mechanism in the latter case too, as outlined in eqn. 8. In the terminology of redox chemistry this is an atom transfer oxidation.

$$ArCH_2-H + O_2NO^-Ce(IV) \rightarrow ArCH_2^{\cdot} + HNO_3 + Ce(III) \quad (8)$$

It finally remains to comment upon the trends observed in the nitrate/acetate (N/A) ratios of Table 2. Baciocchi *et al.*[2] found that under heterogeneous conditions – and most CAN oxidations in acetic acid must be run under such – the N/A ratio depended upon the amount of solid CAN dispersed in the liquid phase, indicating that the oxidation of the benzylic radical can also occur at the surface of the solid. The only experiment run under homogeneous conditions (mesitylene) gave an N/A ratio of 1.5 ± 0.2 at $[NO_3^-] = 0.048$ M (this concentration is calculated on the basis that $[(O_3N)_6Ce(IV)]^{2-}$ is fully dissociated and thus represents a maximum concentration; obviously, this is not the case). This is to be compared with the N/A ratio in the anodic experiment,[7] 1.0 ± 0.3 at $[NO_3^-] = 0.4-1.25$ M. Superfluously, this indicates a higher selectivity in the homogeneous experiment with CAN, since $[NO_3^-]$ is at least 10 times lower. It is, however, not advisable to take N/A ratios from anodic experiments as unambiguous expressions of the reactivity of a carbocation *vs.* nitrate ion and acetic acid, respectively, because of other types of inter-

face phenomena, empirically well documented but still little understood.[5a] In the case of nitrate, as little as 0.002 M [NO_3^-] in 0.2 M [AcO^-] in acetic acid gives an N/A ratio of *ca.* 0.3 in the anodic oxidation of mesitylene;[7] a further increase of [NO_3^-] to 0.02 and 0.1 M does not increase the N/A ratio. This is indicative of an adsorption effect which "saturates" the anodic double layer with nitrate ion already at a very low bulk nitrate concentration.

Thus we cannot at present ascribe the differences observed in the N/A ratios between the anodic and CAN experiments to any particular factor or combination of such. It first would be necessary to try to disentangle the "true" N/A ratio for a series of benzylic cations – *e.g.*, by solvolysis of suitable benzylic tosylates in acetic acid/tetraalkylammonium nitrate – so that one can distinguish "normal" N/A values from those affected by factors in the oxidation processes of interest. Only then can we compare and discuss N/A values from CAN and anodic oxidation with some confidence.

EXPERIMENTAL

Materials and methods. Acetic acid (Merck "100 %" reagent) was crystallized twice before use in the small-scale experiments and used directly in the large-scale ones. The solution of tetrabutylammonium tetrafluoroborate in acetonitrile (Merck, reagent grade) used in the electroanalytical experiments was passed through an alumina (Woelm, grade I) column before adding acetic acid. Supporting electrolytes and inorganic reagents were dried at elevated temperature *in vacuo*.

Isodurene (EGA-Chemie, technical quality, 85+ %) was purified by means of a previously reported sulfonation-desulfonation method.[53] This is necessary in order to remove durene which is a significant impurity even in high-quality commercial samples.

GLC analyses were performed on an HP 5830 gas chromatograph equipped with the HP 18850A GC Terminal. The column used to separate the isomeric acetates was an FFAP 3 % on Gaschrom Q 100/120 mesh column (temperature program, 80 – 240 °C at 8 K min^{-1}). Preparative GLC separation was achieved on a Varian Autoprep A-700 instrument using a 6 m × 10 mm Carbowax 20M column at 180 °C. For other instrumental methods, see references to recent work from this laboratory.[6]

The electroanalytical work was done at the Department of Organic Chemistry, the Norwegian Institute of Technology, Trondheim, Norway using equipment described elsewhere.[54] Small-scale electrolyses were run at constant current using an AMEL Mod. 552 potentiostat as power supply.

Small-scale electrolytes in acetic acid/tetrabutylammonium tetrafluoroborate or potassium acetate. With platinum as electrode material, the cell consisted of a 20 ml water-jacketed flat-bottomed vessel, equipped with a platinum foil (6.3 cm^2) anode and a platinum wire cathode. No cell divider was used. In a typical experiment isodurene (0.50 ml, 0.032 mol) was added to 15 ml of the appropriate solvent/supporting electrolyte. Current (c.d. 10 mA cm^{-2}) was passed through the cell until the required amount of charge had been delivered. Work-up and analysis were done by addition of water (100 ml) and ether extraction, adding a weighed amount of hexamethylbenzene (purified by recrystallization from light petroleum) as an internal standard for gas chromatography.

With graphite as anode material a similar but larger cell was used with a 10 cm^2 graphite anode.

CAN and anodic oxidation in acetic acid/tetrabutylammonium nitrate. CAN oxidation experiments were run so as to simulate the anodic ones as closely as possible. As an example, isodurene (2.0 ml, 0.0133 mol) was reacted with CAN (0.00266 mol; 10 % of the stoichiometric amount) in acetic acid (65 ml) in a jacketed vessel, kept at 56 °C by vapors of refluxing acetone. The orange colour of CAN generally disappeared within 30 min. Work-up was effected by addition of water (*ca* 100 ml), and extraction (twice) with dichloromethane or light petroleum. The extracts were washed with water and dried with magnesium sulfate. After evaporation of the solvent, the N/A ratio was analyzed by ^1H NMR spectroscopy. The remaining part of the product was then refluxed in acetic acid/2 M potassium acetate (25 ml) for 24 h in order to convert the benzylic nitrates into acetates. Work-up and analysis were done as described above.

The electrochemical experiment was performed with isodurene (2.0 ml, 0.0133 mol) in acetic acid (65 ml) containing tetrabutylammonium nitrate (0.016 mol) at 56 or 20 °C. The area of the platinum anode was 30 cm^2 and the c.d. 4.7 mA cm^{-2} and the reaction was run until 0.2 F mol^{-1} had passed. Generally, no cell divider was used, since a separate experiment showed that it had no effect on the product distribution (expt No. 13 in Table 2). Work-up and analysis were done as in the CAN experiments.

Large-scale anodic oxidation of isodurene. Isodurene (45 ml, 0.30 mol) was oxidized anodically in acetic acid (1500 ml) with tetrabutylammonium tetrafluoroborate (30 g) as the supporting electrolyte in a concentric capillary gap cell.[55] The c.d. was 20 mA cm^{-2}

and 2 F mol^{-1} of charge was passed. The acetic acid and isodurene were then distilled off, first at atmospheric pressure and toward the end *in vacuo*. Continued vacuum distillation in a Fischer Spaltrohr column of *ca.* 40 theoretical plates gave 2,4,6-trimethylbenzyl acetate (*1*) in 95 % purity (13.0 g). From the following fractions were isolated 2,3,5- and 3,4,5-trimethylbenzyl acetate (*2* and *3*) by means of preparative gas chromatography. The identity of the three isomers was established by comparison with literature NMR data.[2]

In order to prepare the nuclear substitution product, 2,3,4,6-tetramethylphenyl acetate (*4*), a similar reaction was run with potassium acetate as the supporting electrolyte. After isolation of the crude product, hydrogenation in a Parr glass apparatus at 3–4 atm. for 12 h in acetic acid with 10 % Pd on carbon as catalyst converted the benzylic acetates into the parent hydrocarbon (isodurene), leaving *4* behind. Work-up in the usual manner gave 3.2 g of crude *4*, which after recrystallization from acetone-water exhibited NMR and MS characteristics in accordance with this structure.

Calculations of E^* were performed on a programmable pocket calculator (Texas Instruments Model 59 with the PC-100 B Printer). Execution takes 20–30 min per value. A copy of the program is available from the author (L.E.) on request.

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