

THE CATALYSIS OF THE ELECTROCHEMICAL REDUCTION OF ALKYL BROMIDES BY NICKEL COMPLEXES: THE FORMATION OF CARBON—CARBON BONDS

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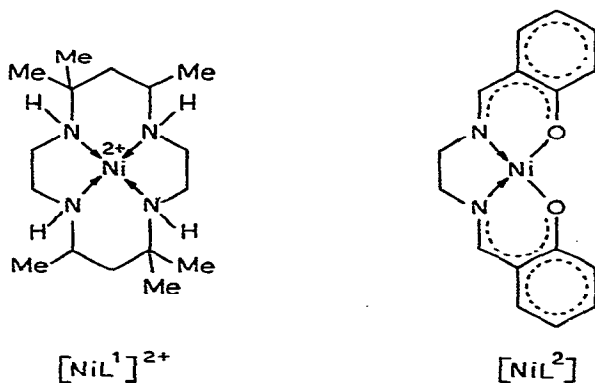
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Summary

The square planar, macrocyclic nickel complex, *N,N'*-ethylenebis(salicylidene-iminato)nickel(II), is shown to be an effective catalyst for the electrochemical reduction of substituted alkyl bromides; this indirect cathodic reduction can lead to a good yield of dimeric products. The reduction of alkyl bromides in the presence of an activated olefin is shown to lead to mixtures of products compatible with radical addition to the double bond. The mechanism of the reaction of nickel(I) complexes with alkyl bromides is discussed in the light of these results.

An earlier paper [1] reported a study of the reduction of two square planar macrocyclic nickel complexes, $[\text{NiL}^1]^{2+}$ and $[\text{NiL}^2]$, and the reaction of the



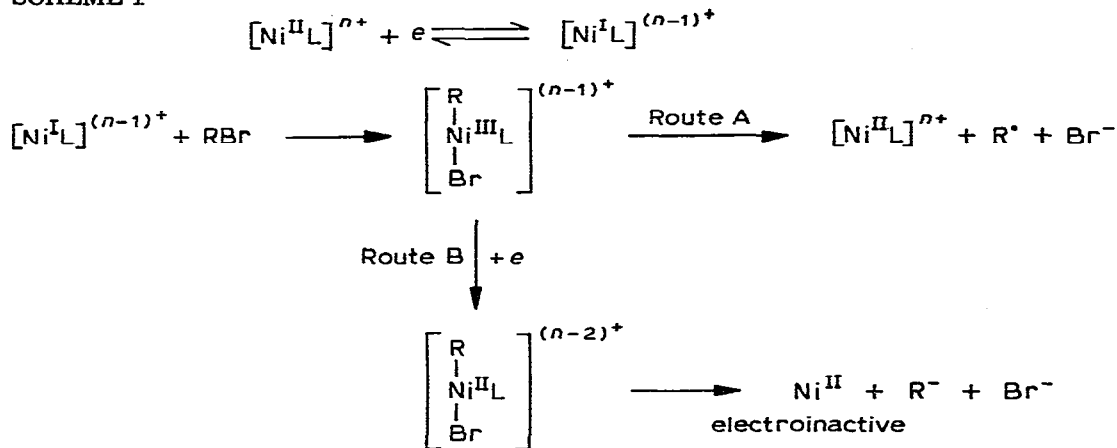
resulting nickel(I) complexes with alkyl bromides. It was shown that a low concentration of both complexes, $[\text{NiL}^1]^{2+}$ and $[\text{NiL}^2]$, would catalyse the complete cathodic reduction of several alkyl halides in aprotic solvents and that in

these reactions the products were consistent with free radical intermediates. The exception was the reduction of primary alkyl bromides in the presence of $[\text{NiL}^1]^{2+}$ where only one molecule of alkyl bromide/molecule of complex reacted and the organic products seemed to be derived from carbanion intermediates. The experimental evidence clearly rules out reaction 1 and a mechanism



involving an organometallic intermediate (see Scheme 1) was proposed, the stability of the Ni—C bond determining the final products. The strength of the Ni—C bond depends on both the macrocyclic ligand and the nature of the alkyl group.

SCHEME 1



A second paper [2] discussed the reduction of $[\text{NiL}^1]^{2+}$ in the presence of an alkyl bromide and an activated olefin and with acrylonitrile and ethyl acrylate a single organic product was isolated (R = n-Bu, s-Bu, t-Bu). These products were compatible with insertion of the olefin into the Ni—C bond followed by reductive cleavage to a carbanion (route B) and the reactions also terminated after the reduction of one molecule of BuBr/molecule of complex and the passage of 2*F*/mol of complex. Hence it was proposed that the electron withdrawing group (CN, COOC₂H₅) attached to the C atom stabilised the Ni—C bond and favoured route B compared to route A.

In this paper the use of $[\text{NiL}^2]$ to catalyse the reduction of substituted alkyl bromides and the reduction of alkyl bromides in the presence of two activated olefins is reported. It is shown that the macrocyclic ligand is very important in determining the reaction pathway and that such systems may be applied in synthesis to the formation of C—C bonds.

Results

The $[\text{NiL}^2]$ catalysed reduction of substituted alkyl bromides

It has previously been shown that the reduction of $[\text{NiL}^2]$ in acetonitrile (AN) is a reversible 1*e* process leading to an anion which is stable and does not reduce further within the potential range of the solvent. This can also be seen

from the cyclic voltammogram of $[\text{NiL}^2]$ shown as curve (a) in Fig. 1. A series of further cyclic voltammograms were run during the stepwise addition of ethyl-3-bromopropionate to the solution of the nickel complex; curves (b) and (c) of Fig. 1 and the data in Table 1 summarise the results. It can be seen that even after the addition of a low concentration of the electrophile, the anodic peak for the reoxidation of $[\text{NiL}^2]^-$ is no longer observed. At the same time the peak current for the cathodic process ($I_{\text{P}}^{\text{Ni}+\text{RBr}}$) has increased compared to that for the complex alone (I_{P}^{Ni}) and this peak current continues to increase on further addition of the alkyl halide. No new reduction peaks are observed but at potentials just positive to zero two anodic peaks for the oxidation of bromide to tribromide and bromine do appear. Ethyl-3-bromopropionate alone does not reduce on Pt below -2.2 V.

The cyclic voltammogram of the solution with a low concentration of ethyl-3-bromopropionate would indicate that the reaction of $[\text{NiL}^2]^-$ with the electrophile is rapid and the substantial increase in the cathodic peak at high concentrations of the alkyl bromide would suggest that the chemical process regenerates the electroactive nickel(II) complex. It should be noted in curve (b) of Fig. 1, however, that the ratio $I_{\text{P}}^{\text{Ni}+\text{RBr}}/I_{\text{P}}^{\text{Ni}}$ is only slightly more than one and hence the reaction of $[\text{NiL}^2]^-$ with the electrophile does not immediately regenerate $[\text{NiL}^2]$.

The cyclic voltammetry experiments were repeated with n-octyl bromide and three other substituted alkyl bromides and essentially similar results were obtained in each case. The ratios of $I_{\text{P}}^{\text{Ni}+\text{RBr}}/I_{\text{P}}^{\text{Ni}}$ are reported for three ratios of complex: electrophile in Table 1. The ratios depend on the structure of the alkyl bromide and reflect the relative rates of the chemical sequences regenerating $[\text{NiL}^2]$. It can be seen that the catalytic cycle is most rapid with 2-bromoethyl acetate and both 3-bromopropionitrile and ethyl-3-bromopropionate cause more rapid regeneration of the nickel(II) complex than the unsubstituted octyl bromide. Certain other related compounds, e.g. ethyl bromoacetate, were also studied but were found to reduce at potentials less negative than the nickel complex; the direct reduction, however, leads to entirely different products.

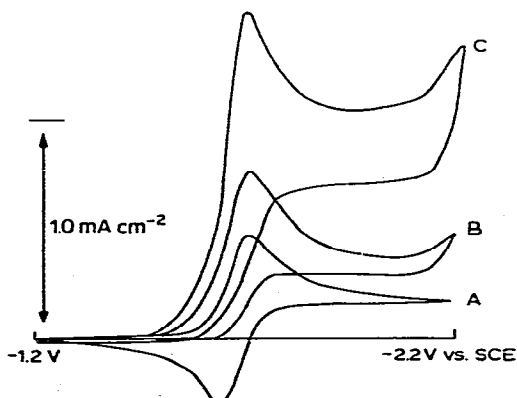


Fig. 1. Cyclic voltammograms for $[\text{NiL}^2]$ (1 mM) in AN/TBAB (0.2 M) containing A. 0 mM, B. 1 mM, C. 10 mM ethyl-3-bromopropionate. Potential scan rate 0.1 V s^{-1} , Pt electrode.

TABLE 1

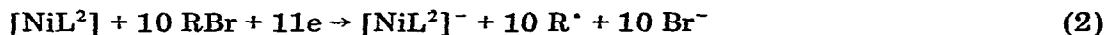
SUMMARY OF DATA TAKEN FROM CYCLIC VOLTAMMOGRAMS FOR $[\text{NiL}^2]$ IN $\text{AN}/\text{Bu}_4\text{NBF}_4$ CONTAINING THREE EXCESSES OF ELECTROPHILES (Pt electrode. Potential scan rate 0.1 V s^{-1} . Concentration of nickel complex 1 mM)

Electrophile	$I_p^{\text{Ni} + \text{RBr}}/I_p^{\text{Ni}}$ for different molar ratios of complex/electrophile ^a		
	1/10	1/50	1/100
n-C ₈ H ₁₇ Br	1.4	2.3	3.9
BrCH ₂ CH ₂ COOC ₂ H ₅	2.9	4.7	5.7
BrCH ₂ CH ₂ CN	2.8	5.4	8.0
BrCH ₂ CH ₂ C ₆ H ₅	1.7	2.4	2.5
CH ₂ COOCH ₂ CH ₂ Br	11.2	18.9	28.5

^a I_p^{Ni} \equiv peak current for the reduction of $[\text{NiL}^2]$ in the solution containing only complex. $I_p^{\text{Ni} + \text{RBr}}$ \equiv peak current for the reduction of $[\text{NiL}^2]$ in the solution containing complex and electrophile.

Controlled potential electrolyses were carried out on solutions (20 mM) of $[\text{NiL}^2]$ and each of the five electrophiles listed in Table 1 (200 mM). In each case, the current was monitored as a function of the charge passed during the electrolysis and when the current had dropped a low value, the organic products were extracted and determined. The current-charge data were used to find the number of electrons per molecule of complex consumed in the complete electrolysis. The results from these experiments are summarised in Table 2.

For 1-bromooctane, ethyl-3-bromopropionate, 2-bromoethylbenzene and 3-bromopropionitrile, the overall reaction follows equation 2 and the major



product is formed by dimerisation of the radical. Disproportionation and hydrogen atom abstraction products are also isolated and, indeed, these are more important with the substituted compounds than with 1-bromooctane. All the data, however, seems consistent with the mechanism of Scheme 1, route A.

The coulometry and products from electrolysis with bromoethyl acetate indicate that although the corresponding products are isolated in minor amounts, there must be a competing and more important $2e/\text{molecule}$ of bro-

TABLE 2

PRODUCTS FROM THE $[\text{NiL}^2]$ CATALYZED REDUCTION OF THE ALKYL HALIDES, $\text{XCH}_2\text{CH}_2\text{Br}$, AT -1.75 V vs. SCE (Ratio complex/electrophile 1/10 in $\text{AN}/\text{Bu}_4\text{NBF}_4$, Pt cathode)

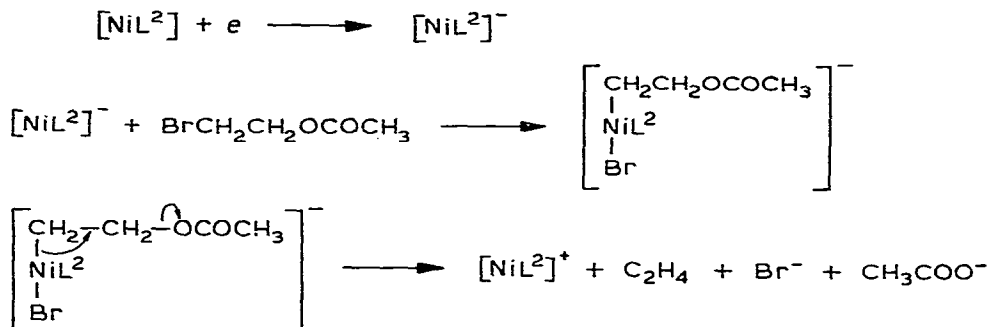
X	n-value F/mol complex	product organic yield of (%)		
		$(\text{XCH}_2\text{CH}_2)_2$	$\text{XCH}=\text{CH}_2$	XCH_2CH_3
n-C ₆ H ₁₃	11.3	77	4	6
COOC ₂ H ₅	11.1	63	9	28
CN	11.4	30	6	10
C ₆ H ₅	11.3	57	22	16
OCOCH ₃ ^a	17.5	4	10	10

^a Major product 1,2-ethanedioldiacetate 21%.

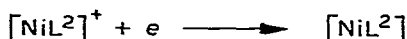
moethyl acetate route which gives some 1,2-ethanedioldiacetate. Since this product is probably formed by reaction 3 in the aprotic medium, the two elec-



tron reaction of Scheme 2 seems reasonable. Certainly the acetate is well placed to act as a leaving group in the decomposition of the nickel-carbon bonded intermediate and the ethylene would be lost during electrolysis.



SCHEME 2



[NiL²] catalysed reduction of butyl bromides in the presence of activated olefins.

Figure 2 illustrates the cyclic voltammetric behaviour of the $[\text{NiL}^2]/t\text{-BuBr}/\text{CH}_2\text{CHCN}$ system and the important data taken from these voltammograms are summarised in Table 3. On addition of a large excess of *t*-butyl bromide to the solution containing the nickel complex, the cathodic peak current increases substantially and the anodic peak is no longer observed. The addition of acrylonitrile to this solution has little effect on the peak current density but it does cause some deterioration in the peak shape. These experiments were repeated with both primary and secondary butyl bromide and with ethyl acrylate as the olefin and the results were essentially similar. Neither the olefins nor the butyl bromides reduce directly at the Pt cathode below -2.2 V. Cyclic voltammetry showed that the olefins themselves do not react with $[\text{NiL}^2]^-$.

The main products and the n -values found from the controlled potential electrolyses of these systems are reported in Table 4. In all cases the products are a hexyl cyanide (from acrylonitrile) or an ethyl heptanoate (from ethyl acrylate) but other products were found. Firstly with both olefins, some butane, butenes and octane, was observed, although much less than would be expected in the absence of olefin [1]. Secondly some radical initiated polymerisation occurred; with acrylonitrile solid polymer precipitated while with ethyl acrylate and each of the butyl bromides, at least two long retention time products were seen on the GLC trace. These amounted to 20–30% of the product. Their mass spectra showed these molecules to be adducts of one butyl group and two ethyl acrylates although their structures were not determined further. The yields of all products was a function of the ratio of butyl halide to olefin.

These product spectra are typical of those expected for butyl radical addi-

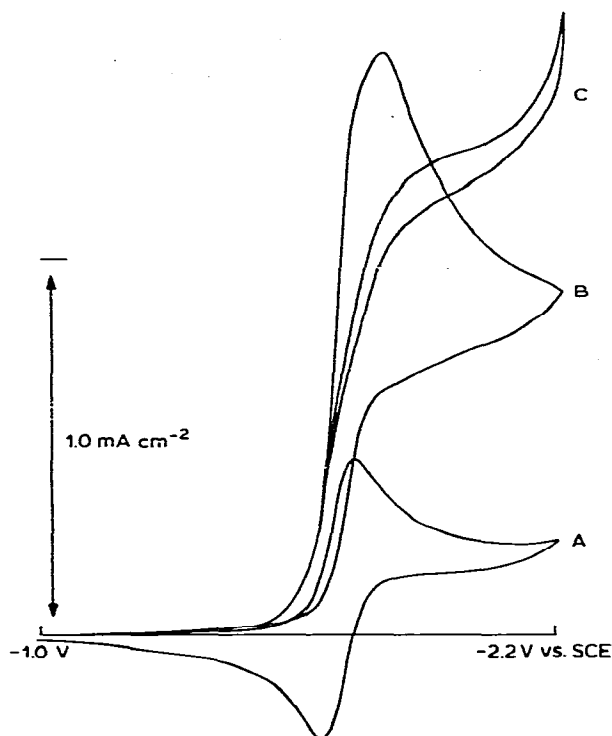
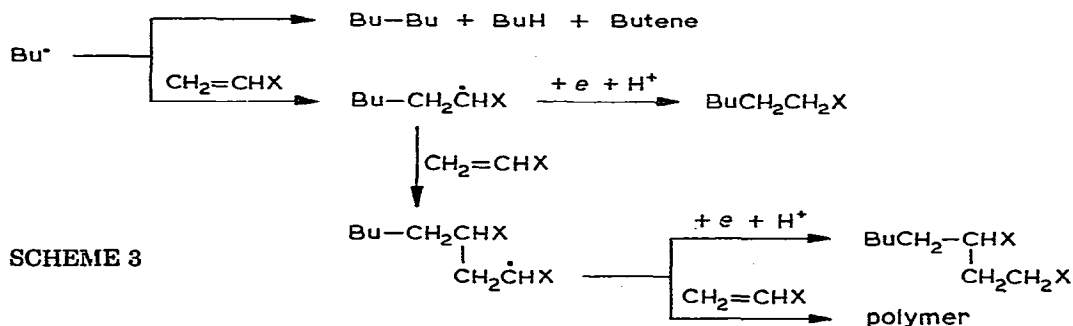
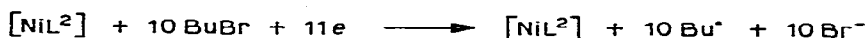


Fig. 2. Cyclic voltammograms for $[\text{NiL}^2]$ (1 mM) in AN/TBAB (0.2 M). A: alone; B: containing *t*-butyl bromide (25 mM); C: containing *t*-butyl bromide (25 mM) + acrylonitrile (50 mM). Potential scan rate 0.1 V s^{-1} , Pt electrode.

tion to activated olefin and taking into account the coulometry the likely mechanism is shown in Scheme 3.



The products will depend on the relative rates of the several competing reactions. It should be noted that the major products from the *t*-butyl bromide electrolyses arise from addition of the butyl radical in the opposite way to that observed for the primary and secondary radicals and that shown in Scheme 3.

TABLE 3

DATA TAKEN FROM CYCLIC VOLTAMMOGRAMS IN AN/ Bu_4NF_4 (Potential scan rate 0.1 V s^{-1} , Pt electrode)

Solution	I_p (mA cm^{-2})	Reversibility of $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$
$[\text{NiL}^2]$ (1 mM)	0.31	rev
$[\text{NiL}^2]$ (1 mM) + CH_2CHCN (100 mM)	0.31	rev
$[\text{NiL}^2]$ (1 mM) + $(\text{CH}_3)_3\text{CBr}$ (50 mM)	2.7	irrev
$[\text{NiL}^2]$ (1 mM) + $(\text{CH}_3)_3\text{CnR}$ (50 mM) + CH_2CHCN (100 mM)	2.6	irrev


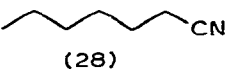
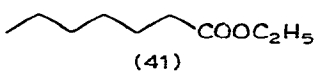
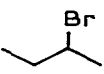
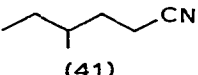
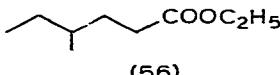

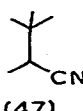
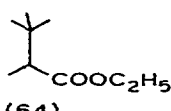
This is presumably due to a kinetic effect and the reversibility of t-butyl radical addition to the olefin. A low yield (2–4%) of the terminal addition product was also observed.

Discussion

The direct electrochemical reduction of the alkyl bromides studied in this paper generally requires a potential more negative than -2.2 V . In the presence of a low concentration of the nickel complex, however, the reduction takes place at -1.75 V and therefore $[\text{NiL}^2]$ must be regarded as an effective catalyst for the reduction of alkyl bromides. On the other hand, the current densities for the $[\text{NiL}^2]$ catalysed reductions are low and, for example, the peak current densities from the cyclic voltammograms of solutions of 1 mM complex + 100 mM primary alkyl bromides (see Table 1) vary between 2 and 30% of those estimated [3] for a process controlled by the rate of diffusion of the alkyl halide

TABLE 4

MAIN PRODUCTS FROM THE $[\text{NiL}^2]$ CATALYSED REDUCTION OF THE BUTYL BROMIDES IN THE PRESENCE OF OLEFIN $[\text{NiL}^2]/\text{RBr}/\text{CH}_2\text{CHX} \equiv 1/10/50$

RBr	CH_2CHCN		$\text{CH}_2\text{CHCOOC}_2\text{H}_5$	
	$nF/\text{mol}[\text{NiL}^2]$	Product (yield ^a)	$nF/\text{mol}[\text{NiL}^2]$	Product (yield ^a)
	15	 (28)	16	 (41)
	18	 (41)	20	 (56)
	17	 (47)	19	 (64)

^a % based on butyl bromide.

to the electrode surface. The current is limited by the rate of the chemical sequence regenerating $[\text{NiL}^2]$ from $[\text{NiL}^2]^-$ and clearly this is dependent on the structure of the alkyl group and the structure of the macrocyclic ligand as well as the solution conditions. Conditions for increasing this current density are under investigation.

The $[\text{NiL}^2]$ catalysed reduction of most substituted primary alkyl bromides leads to acceptable yields of the dimeric products. Moreover, the reactions continue until all the alkyl bromide is consumed. The products from the reduction of 2-bromoethyl acetate are disappointing from a synthetic point of view, but they provide additional evidence for an intermediate with a metal-carbon bond.

The electrolyses of solutions containing a butyl bromide and an activated olefin also provide evidence for a free radical intermediate. The product spectrum is quite unlike that observed with $[\text{NiL}^1]^{2+}$ as the catalyst and typical of that for radical addition to an olefin. The cyclic voltammograms for $[\text{NiL}^2] + \text{RBr}$ are also almost unchanged by the addition of the olefin (cf. $[\text{NiL}^1]^{2+} + \text{RBr} + \text{olefin}$) [2] confirming that the basic reaction between the $[\text{NiL}^2]^-$ and the alkyl bromide remains the same. It should also be noted that the organic intermediate is formed away from the electrode surface and this is in contrast to the direct electrochemical reduction where the reactions are commonly less selective with products arising from carbanion, radical and at some cathodes, metal alkyl intermediates [4,5].

Hence all experiments with $[\text{NiL}^2]$ are compatible with the reaction mechanism in Scheme 1, route A. This would indicate that the Ni-C bond formed with this complex is much weaker than that with the complex $[\text{NiL}^1]^{2+}$; it cleaves spontaneously and never has a sufficient lifetime for an insertion reaction to occur. With $[\text{NiL}^1]^{2+}$, the lifetime of the Ni-C bond depends on the nature of the alkyl group; it is increased by electron withdrawing groups (e.g. CN, COOC_2H_5) and decreased by electron donating groups (e.g. CH_3) attached to the C atom. Moreover, the rate of the insertion reaction depends on the nature of the inserting olefin and it is fastest for terminal olefins with an electron withdrawing group.

Experimental

Ethyl-3-bromopropionate, 2-bromoethyl benzene, 2-bromoethylacetate and ethyl acrylate were supplied by Aldrich Chemicals Ltd. and 3-bromopropionitrile by Koch Light Ltd. All other alkyl bromides and acrylonitrile were obtained from BDH Ltd. The preparation of the solvent, base electrolyte and the nickel complexes has been described earlier as have the instrumentation, cells and experimental procedures [1,2].

At the end of the electrolysis, a suitable internal standard was added to the catholyte and the solution poured into 400 cm³ of saturated aqueous sodium chloride. The organic products were extracted with three aliquots of ether, and after washing with water, the ether was dried with anhydrous magnesium sulphate and reduced to a small volume. The final ether solution was analysed by GLC and GLC-mass spectroscopy. Most products were identified by comparison of retention time and mass spectra with standard samples from BDH Ltd,

Koch Light Ltd. or Aldrich Chemicals Ltd. The exceptions were: (a) The major product from 2-bromoethyl acetate. This was isolated by preparative scale GLC; $^1\text{H NMR } \delta(\text{CHCl}_3 \text{ vs. TMS})$: 2.1 (6H, s), 4.3 (4H, s). IR $\nu(\text{cm}^{-1})$ film: 2975, 1740, 1390, 1240, 1160. (b) The major products from electrolysis of the bromobutanes in the presence of activated olefin. The branch chain products were compared with samples supplied by Healy [2]. (c) The long retention time products from the electrolyses of the butyl bromides in the presence of ethyl acrylate. The mass spectra were from 1-bromobutane: m/e (%) 214 (6), 213 (49), 188 (24), 166 (38), 114 (80), 88 (44), 55 (98), 41 (100) and m/e (%) 157 (1), 141 (3), 114 (9), 96 (100), 69 (22), 68 (36), 55 (17), 41 (79). 2-Bromobutane: m/e (%) 214 (4), 213 (60), 201 (9), 188 (49), 155 (77), 114 (100), 88 (17), 55 (68), 41 (74) and m/e (%) 141 (4), 114 (10), 97 (7), 96 (100), 69 (20), 68 (34), 55 (16), 41 (69). *t*-Butyl bromide: m/e (%) 243 (3), 214 (7), 213 (65), 201 (37), 188 (4), 155 (58), 128 (83), 101 (49), 57 (100) and m/e (%) 157 (18), 128 (11), 115 (13), 114 (11), 96 (100), 68 (30), 55 (18), 41 (57).

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