

# Electropolymerization of butyl isocyanate:

## 1. Initiation

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Electrolysis of a solution of n-butyl isocyanate and a quaternary ammonium perchlorate in *NN'*-dimethylformamide at  $<-40^{\circ}\text{C}$  results in the formation of high molecular weight poly(n-butyl isocyanate). Initiation occurs by both direct reduction of the monomer and subsequent dimerization of the radical anion produced and by a two electron reduction of the solvent to produce a symmetrical solvent-reduced dianion analogous to the reduced monomer. The reduced solvent species undergoes protonation to produce glyoxal and dimethyl amine.

### INTRODUCTION

The chemical reactions of the isocyanate group are extremely varied<sup>1,2</sup>. Reaction with nucleophilic reagents containing an active mobile hydrogen atom gives rise to the familiar, industrially-important urethane polymers which have been extensively studied as, to a lesser extent, have the cyclic dimerization and trimerization reactions. Finally, linear homopolymerization and copolymerization reactions produce high molecular weight compounds.

Shashoua<sup>3</sup> first produced a series of polymers from a variety of alkyl and aryl isocyanates. The linkage was shown to be an amide and the polymers were termed nylon-1 by analogy with nylon-6 prepared from caprolactam. Initiating systems reported since that time all show one common factor in that polymerization occurs by an anionic mechanism at relatively low temperatures. Shashoua used the principle of base initiation, the direct attack of the cyanide ion from either sodium or potassium cyanide in dimethylformamide at  $-60^{\circ}\text{C}$ . The reaction is extremely rapid and the polymer is insoluble both in the monomer and the reaction medium. The use of ethyl lithium also falls into this category but this reaction is slow; monomer conversion and molecular weight are reported to increase over several hours<sup>4</sup>. Presumably this difference is due to the extent of dissociation of the propagating ion pairs. It has also been suggested, by analogy with other systems, but with little actual proof, that polymerization may be brought about by direct electron transfer<sup>5</sup>.

Using a variety of reagents including sodium naphthenate, sodium benzophenyl ketone and  $\gamma$  radiation a slow reaction occurs. It is thought that a radical-ion is produced which subsequently dimerizes to produce a dianion, although other reactions particular to the isocyanate group may interfere.

The electropolymerization of isocyanates has received little study. Shapoval<sup>6</sup> has briefly described the polymerization of phenyl isocyanate in dimethylformamide using quaternary ammonium iodide as electrolyte and a platinum cathode. The yield was reported to improve with increase in monomer concentration and decrease with both temperature and current density and that the resulting polymer was crystalline. It has been suggested that this is the first report

of an ordered polymer produced at an electrode surface<sup>7</sup>.

Here, we describe investigations into the electroinitiated polymerization of butyl isocyanate using a variety of techniques and attempts to interpret certain of the rather novel results obtained particularly in the initiation system, which are unique for this class of compound.

### EXPERIMENTAL

#### Materials

*NN'*-dimethylformamide (BDH) was distilled over potassium carbonate at atmospheric pressure ( $154^{\circ}\text{C}$ ), stored over calcium hydride and fractionally distilled when required from calcium hydride under a reduced pressure of argon (3 torr,  $45^{\circ}\text{C}$ ). The fraction used was shown by g.l.c. to be free from dimethylamine.

Butyl isocyanate (Fluka or Ralph N. Emmanuel) was fractionally distilled at normal pressure ( $114^{\circ}-115^{\circ}\text{C}$ ). The fractions were assayed by g.l.c. to show removal of initial impurities (probably carbamoyl chloride) and were retained at  $-20^{\circ}\text{C}$  in the dark.

Tetraethyl ammonium tetrafluoroborate  $(\text{C}_2\text{H}_5)_4\text{N}.\text{BF}_4$  was prepared by adding an aqueous saturated solution of  $(\text{C}_2\text{H}_5)_4\text{NBr}$  to a large excess of a hot aqueous solution of  $\text{NaBF}_4$ . Cooling to  $0^{\circ}\text{C}$  gave rise to crystals of  $(\text{C}_2\text{H}_5)_4\text{N}.\text{BF}_4$ . The crystals were filtered, washed with ethanol and dried at  $50^{\circ}\text{C}$ . The yield was limited to 20% since further crystallization produced plates of  $\text{NaBF}_4$ . The product was assayed both qualitatively for the absence of  $\text{Na}^+$  and  $\text{Br}^-$  and gravimetrically for purity via the tetralkyl ammonium cation and the tetrafluoroborate anion.

Tetraethyl ammonium perchlorate  $(\text{C}_2\text{H}_5)_4\text{N ClO}_4$  was prepared by digesting tetraethyl ammonium bromide with perchloric acid (70%). Volatile  $\text{HBr}$  and excess  $\text{HClO}_4$  were removed under vacuum. The salt was filtered, washed with a minimum of water dried and recrystallized from ethanol.

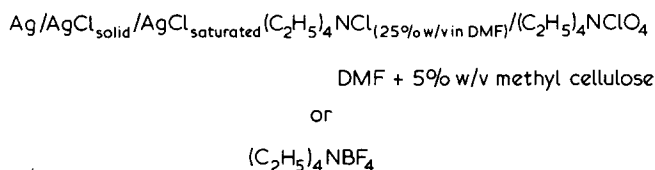
#### Equipment

Electrolyses at constant current were carried out using a constant current unit capable of supplying current in steps

of 1 mA to a maximum of 50 mA and manufactured by Sandmar Electronic Products Ltd.

Experiments carried out at constant potential were made using a 1.6 A potentiostat manufactured by the Chemical Electronics Co. Ltd; its overall operation was limited to a cell voltage of 100 V. For use in cyclic voltametric experiments a waveform generator (Chemical Electronics Co. Ltd model RB1) was connected to the external input of the potentiostat, enabling a sweep voltage of up to  $\pm 3$  V to be applied to the cell at a series of speeds of between 0.01 and 1000  $\text{V s}^{-1}$ . The potential scan could have a single or a continuous cycle. The output of the waveform generator was modified to give a second identical output which was fed into the X-axis input of the X-Y recorder (Bryans 2604) whilst the Y-axis was the current response from the monitoring amplifier of the potentiostat.

For the voltammetric work a reference electrode was developed, based on the Ag/AgCl system and contained in a glass tube 1 cm<sup>2</sup> diameter and fitted with a No. 4 glass sinter, the complete system being:



A variety of cells were used for electrolysis, all based on a design in which the anode and cathode compartments are separated by a sintered glass frit. Mercury was used as the cathode material to allow comparison of the results with those reported by Shapoval using polarographic techniques. The anode was a platinum foil. For analytical work, either the normal reference electrode and Luggin capillary or a quasi-reference electrode consisting of a platinum wire were used. The analytical cells were small enough to fit inside a Dewar vessel containing a freezing mixture maintained at  $-60^\circ\text{C}$ .

Great care was taken in preparing the solutions for electrolysis. All containers were flamed before use. A known amount of dried electrolyte was placed in a solvent vacuum transfer vessel into which, via a burette built into the distillation system, a known amount of solvent was added, to produce a 0.1 M solution. Known amounts of monomer were transferred (inside a dry box) to the cell to which was added the previously measured solvent/electrolytic solution — all operations being carried out in an atmosphere of dried argon.

## RESULTS AND DISCUSSION

In the electropolymerization of phenyl isocyanate reported by Shapoval<sup>6</sup>, the yield of polymer was said to increase on reducing the current density below 0.1 mA  $\text{cm}^{-2}$  when no polarization of the platinum electrode occurred. Accordingly several attempts at polymerization were made at this current density in a divided cell containing a solution of butyl isocyanate in DMF using tetraethyl ammonium tetrafluoroborate as the supporting electrolyte. No polymer was produced even after 24 h electrolysis at  $0^\circ\text{C}$ . Increasing the current density to 10 mA  $\text{cm}^{-2}$  gave rise to polymer on the cathode surface within 1 h; however, this interrupted the flow of current. Attempts to remove the polymer from the electrode surface by mechanical and electrical pulse treatments during the electrolysis proved unsuccessful. A similar

polarization occurred using mercury as cathode, but a larger electrode surface area and vigorous stirring produced conditions whereby polymerization occurred in the bulk of the solution to yield a system capable of kinetic treatment.

Attempts at polymerization using constant potential at the reduction potential of the solvent and using vigorous stirring were unsuccessful because slight changes in the electrical resistance between the reference and working electrodes caused by solution turbulence made the operation of the potentiostat quite impossible. However, analysis of the reaction mixture showed the presence of small but significant amounts of the cyclic butyl isocyanate trimer.

A series of experiments in which the temperature was decreased showed that at  $-40^\circ\text{C}$  polymerization only occurred at both platinum and solid mercury electrodes. Additionally the successful use of platinum eliminated the possibility that an amalgam of mercury with the tetraethylammonium cation was responsible for initiation.

Passage of a current of 50 mA for 45 min through a solution of solvent (DMF) and electrolyte followed by the immediate addition of monomer resulted in an extremely rapid polymerization. This indicates the formation, in the solvent, of some active but transitory species. A lapse of 15 min following electrolysis prior to monomer addition resulted in no polymerization occurring. Similarly a higher current passed for a shorter time was more effective than passing the same number of coulombs over a longer time period.

Cyclic voltammetry was used to elucidate the nature of this transitory species. A typical voltammogram is shown in Figure 1, where the solid curve is the current response when a potential scan is applied to a solution of the electrolyte and solvent only. The broken curve is obtained when butyl isocyanate is present in the mixture and the scan is reversed at  $-2.4$  V to avoid the background peak. The dotted curve illustrates the effect of added water. The isocyanate peak B occurs at  $-2.6$  V versus the reference electrode:



The background peak begins to appear on the trace as the potential approaches  $-2.4$  V (peak C') but it is well resolved from the isocyanate peak. There is no indication of a reverse peak, implying that the product of reduction is completely removed in the 5 s required for the potential, at this scan rate, to return to  $-2.16$  V. Alternatively, the reverse re-oxidation has a low rate constant, or in electrical terms a low

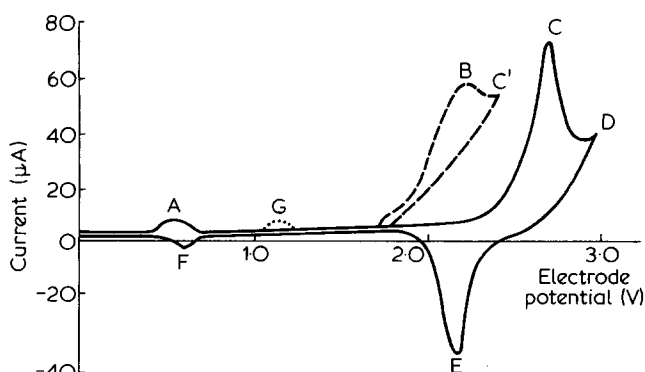


Figure 1 Cyclic voltammogram. Cathode, Hg; anode, Pt; scan rate 0.1  $\text{V s}^{-1}$  —, 0.1 M  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  in DMF; — —, 0.1 M  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  + 0.01M  $\text{C}_4\text{H}_9\text{NCO}$  in DMF; ···,  $1 \times 10^{-4}$  M water added

transfer coefficient,  $\beta$ , ( $\alpha$  in the case of reduction), implying that the electron transfer is the rate controlling process and is irreversible.

The transfer coefficient is proportional to the potential which assists in the reduction or oxidation. It can be expressed in terms of the theory of absolute reaction rates<sup>8</sup>. For reduction:

$$V_R = k_R C_0^e \exp(-U_R - \alpha n e E) / kT \quad (1)$$

where  $V_R$  is the rate of reduction;  $C_0^e$  = the electrode concentration in the oxidized form;  $n$  = the number of electrons transferred in the activation step;  $\alpha$  = the transfer constant – the proportion of the potential which assists the reduction;  $U_R$  = the activation energy of the reduction;  $e$  is the charge on the electron and  $k$  the Boltzmann constant; and  $E$  = the applied potential.

Applying the relationship  $e/k = F/R$  (where  $F$  is the Faraday) and incorporating  $\exp(-U_R/kT)$  in  $k_R$  then:

$$V_R = k'_R C_0^e \exp(-\alpha n F E / RT) \quad (2)$$

A similar expression applies for oxidation:

$$V_0 = k'_0 C_R^e \exp(\beta n F E / RT) \quad (3)$$

where  $\beta$  is the transfer constant for oxidation such that

$$\alpha + \beta = 1$$

The value of  $\alpha n$  can be obtained by several methods and since  $n$  is a small integer, so can the value of  $\alpha$ . This also applies to  $\beta$  for the oxidation curve.

An approximate value of  $\alpha n$  can be obtained from the semi-empirical relationship:

$$\alpha n = \frac{0.048}{E_p - E_{p/2}} \quad (4)$$

where  $E_p$  and  $E_{p/2}$  refer to the peak potential and half-peak potential, respectively. From Figure 1,  $\alpha n = 0.30$ . Assuming  $n$  to be unity,  $\alpha = 0.30$  which is in reasonable agreement with the results of Shapoval<sup>9</sup> who obtained 0.34–0.5 from polarographic measurements using phenyl isocyanate. To confirm this value, and to determine that diffusion only was occurring during the cycle, values of the peak current ( $i_p$ ) were determined over 400 s at  $-2.16$  V. Up to 100 s the value of  $it^{1/2}$  remained constant at  $56.7 \pm 0.004 \mu\text{A s}^{-1/2}$ , the value increasing continuously after 120 s. Additionally, no significant error due to Faradaic loss was present, in that values of  $i_p/V^{1/2}$  versus  $V^{1/2}$ , where  $V$  is the scan rate in  $\text{V s}^{-1}$ , remained constant at  $183.45 \pm 1.4 \mu\text{A s}^{-1/2}$ .

The theoretical treatment of a potential versus current curve involves a simultaneous solution for the concentration of the active species at the electrode from a modified Nernst equation and for the rate of diffusion at a plane electrode. In the Nicolson and Shain<sup>10</sup> analysis for the former, the final result is:

$$i = nFAC^b (\pi Da)^{1/2} \chi \quad (5)$$

where  $A$  is the area of the electrode,  $C^b$  the bulk concentration of the component undergoing reaction,  $D$  the diffusion coefficient and  $a = nVF/RT$ ;  $V$  is the rate of change of potential and  $\chi$  a 'current function' parameter which is depen-

dent on the value  $(E_t - E_0)/n$  where  $E_t$  is the potential at time  $t$  and  $E_0$  the standard electrode potential.

At the maximum of the scan the current becomes, for the reversible case:

$$i_p = Kn^{3/2} AD^{1/2} C^b V^{1/2} \quad (6)$$

and for their reversible case:

$$i_p = Kn(\alpha n)^{1/2} AD C^b V^{1/2} \quad (7)$$

where the constant  $K$  is the Randles–Seveik constant, which for the reversible case equals 272 if  $C^b$  is in  $\text{mol l}^{-1}$ ,  $V$  in  $\text{V s}^{-1}$  and  $D$  in  $\text{cm}^2 \text{s}^{-1}$ . If equation (5) is combined with the equation derived for the semi-finite linear diffusion current at a plane electrode<sup>11</sup>:

$$i = \frac{nFAC^b D^{1/2}}{\pi^{1/2} it^{1/2}} \quad (8)$$

then

$$n^{1/2} = \frac{i_p F}{K^{1/2} it^{1/2} V^{1/2}} \quad (9)$$

and

$$n = \frac{3.34 \times 10^{-2}}{V} (i_p / it^{1/2})^2$$

for the irreversible case or

$$n = \frac{4.05 \times 10^{-2}}{V} (i_p / it^{1/2})^2$$

for the reversible case which can be used to determine  $n$  using the mean values of  $i_p/V^{1/2}$  and  $it^{1/2}$  previously mentioned, resulting in a value of  $n = 0.3942$ .

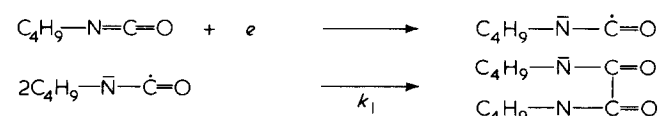
It is also possible to measure  $\alpha n$  by measuring the shift in the peak potentials at varying scan rates by use of the equation:

$$E_p^1 - E_p^2 = \frac{0.0128}{\alpha n} \ln V_2 / V_1$$

where  $E_p^1$  and  $E_p^2$  are the peak potentials at scan rates  $V_1$  and  $V_2$ .

Using the experimentally-determined values of  $E_p = 2.25$  V at  $1.0 \text{ V s}^{-1}$  and  $2.19$  V at  $0.1 \text{ V s}^{-1}$ ,  $\alpha n = 0.3275$ .

$\alpha n$  is thus in the range 0.30 to 0.35. Although  $n$  has not actually been calculated it is probably equal to unity. However, the value of  $\alpha n$  is itself useful in indicating that the re-oxidation step has a transfer coefficient  $\beta$  of at least 0.7. Thus a reverse peak would be observed if the reduction product were stable; no such curve is observed. This may be interpreted chemically as:

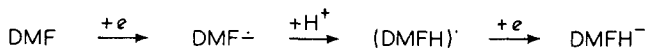


where  $k_1$  is large. From observations of the yield of polymer this dimeric dianion is not particularly susceptible to further polymerization.

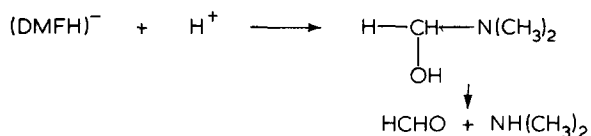
Considering now the background voltammogram due to the solvent, peaks C and E refer to the reduction and oxidation stages, respectively, whilst D would appear to be derived from the electrolyte in that substitution of  $\text{N}(\text{CH}_3)_4$  for  $\text{N}(\text{C}_2\text{H}_5)_4$  caused it to disappear. Experiments also showed the presence of trimethylamine after electrolysis, whilst no triethylamine was detected and the electrolyte  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  could be recovered unchanged.

Application of equation (4) to the reduction peak gives  $\alpha n \equiv 1.2$ . Since  $\alpha < 1$ , then  $n = 2$ , since simultaneous tri-reduction is extremely rare.

For the reverse (oxidation) peak  $\beta n = 0.8$  which would imply a value of  $n = 1$ , which would be the case if the initial reduction occurred by an ECE mechanism, i.e.



The second electron will probably add at the same potential as the first so that if protonation were rapid an apparent two electron reduction would occur. The reverse peak would then be concomitant with a single-reoxidation step. However, present experiments indicate that both reduction and oxidation involve two electrons, for the sum of the two transfer coefficients would then be unity ( $\alpha = 0.6$ ;  $\beta = 0.4$ ). This could be fortuitous, but it is supported by the fact that electrolysis carried out at  $-2.50$  V in the absence of monomer did not produce formaldehyde and also that only one electron is required to produce one molecule of dimethylamine rather than the two postulated previously:



In addition, the peak separation of 430 mV is rather large for the oxidation step to involve only one electron. For such a reaction where  $\alpha = 0.8$ , the peak separation could be expected to be approximately 175 mV.

Equation (7) indicates that the peak height is proportional to  $(\alpha n)^{1/2}$ . If  $n = 2$  for both oxidation and reduction, then:

$$i_p^0/i_p^R = (\beta/\alpha)^{1/2} \quad (10)$$

or

$$i_p^0 = 0.8164 i_p^R \quad (11)$$

Thus if  $i_p^R$  is 77  $\mu\text{A}$  the reverse peak should be about 63  $\mu\text{A}$ . From Figure 1 the value is 47  $\mu\text{A}$ , and clearly some reaction has occurred. Protonation of the intermediate can be discounted since addition of water (curve G) had little effect.

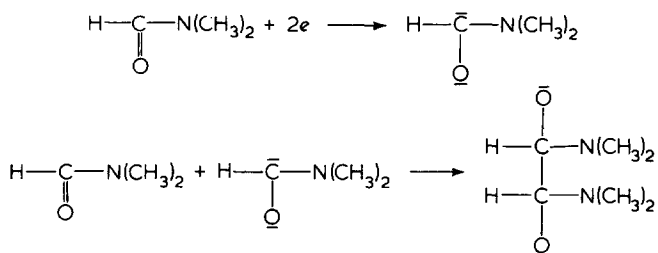
If a first order decay is assumed, then the pseudo-first order rate constant can be evaluated from the time interval between the peaks and the peak current ratio:

$$-\ln \frac{(\text{DMF})_t^{2-}}{(\text{DMF})_0^{2-}} = kt = \frac{-\ln i_p^0}{0.8614 i_p^R} \quad (12)$$

Variation of the scan rate between 0.03 and 1.0  $\text{V s}^{-1}$  gives a mean rate constant of  $2.32 \pm 0.09 \times 10^{-2} \text{ s}^{-1}$ .

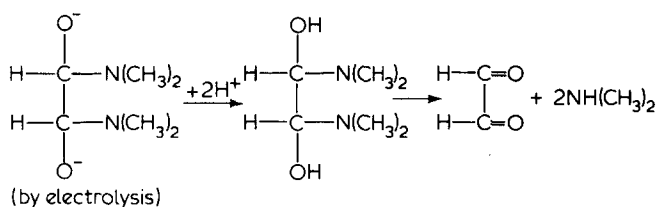
Peaks A and F of Figure 1 occurred in all voltammograms and were not removed by repeated purification of the reagents. No change occurred in the peaks on substituting  $\text{N}(\text{CH}_3)_4$  for  $\text{N}(\text{C}_2\text{H}_5)_4$  nor on exchanging  $\text{BF}_4^-$  for  $\text{ClO}_4^-$ .

A chemical interpretation of peaks C and E indicates that the solvent is first reduced to a dianion which reacts further, almost certainly with the solvent, since there is no change in the electrolyte.



The direduction of a ketone is unusual, the single reduction to the radical anion being more common<sup>12</sup>; this is usually easily protonated so that the second reduction to the dianion occurs only in a medium of low proton availability such as pyridine<sup>13</sup>. This was observed with benzophenone where the dianion was capable of initiating the polymerization of styrene when the anion radical proved to be incapable<sup>14</sup>.

To investigate further the products resulting from the electrolysis of DMF, a constant current electrolysis at 50 mA using solvent and electrolyte only was carried out. Samples were removed during the electrolysis and analysed by g.e.c. using triethylamine as an internal standard. Blank runs indicated that no triethylamine was produced from the discharge of the electrolyte. The results are shown in Table 1. The most plausible mechanism to explain these results can be outlined as:



Thus within experimental error it may be assumed that one molecule of dimethylamine is liberated per electron transferred at the cathode. Glyoxal, however, could not be detected by g.l.c. In order to confirm its possible presence, the electrolysis reaction was simulated by the addition of sodium to DMF which rapidly became yellow and, after a vigorous reaction involving the evolution of volatile material, produced a yellow solid. G.l.c. of the condensate indicated the presence of dimethylamine and unreacted DMF. Mass spectra indicated peaks at  $m/e = 45$  and 74 (dimethylamine and DMF, respectively) together with a peak at 58 which could be ascribed to glyoxal. DMF alone did not produce this peak which could be due to the demethylated DMF ion,  $\text{HCON}(\text{CH}_3)^-$

Table 1 Production of dimethylamine by the electrolysis of DMF 50 mA  $[(\text{C}_2\text{H}_5)_4\text{N}.\text{ClO}_4]$ , 0.1M

Time (h)	Moles dimethylamine		$\frac{B}{A}$
	Calculated $\times 10^3$ (A)	Observed $\times 10^3$ (B)	
1	1.865	1.427	0.765
2	3.73	3.473	0.953
4	7.46	7.176	0.962
8	14.92	14.23	0.954
10	18.65	18.01	0.966

Table 2 U.v. spectra of DPPH electrolysed in DMF

	$\lambda_{\max}$ (nm)	$\epsilon$	$\lambda_{\max}$ (nm)	$\epsilon$
DPPH (initial)	329	5090	516	3977
DPPH (anode)	330	5075	560	610
DPPH (cathode)	329	5250	435	7100
			(490 shoulder*)	

\* May be due to some unreacted DPPH  
0.2 g DPPH in 20 ml DMF divided cell: 0.00046 Faraday

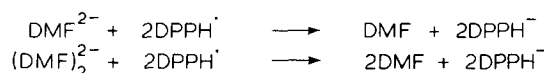
In order to confirm the results obtained from cyclic voltammetry and from e.s.r. measurements, which indicated the absence of DMF radicals, diphenyl picryl hydrazyl (DPPH) was added to the polymerizing system, with the surprising result that both the rate of polymerization and the polymer yields were lower than those normally observed. DPPH, however, is capable of reduction and/or oxidation at an electrode as described by Funt and Grey<sup>15</sup>, who reported the presence of five stable forms of DPPH following electrolysis in tetrahydrofuran:



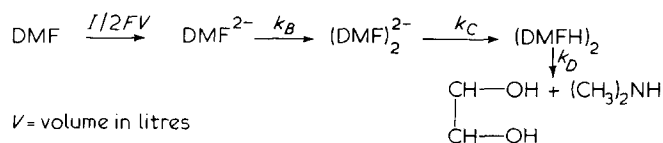
Normal DPPH (I) is converted into (II) or (III) at electrode potentials of about  $\pm 0.3$  V. (IV) and (V) are formed at potentials of about  $-2.0$  V and probably represent the successive reductions of the three nitro groups of the picryl ring system; each nitro group is known to undergo a single reduction<sup>16</sup>.

Electrolysis of DPPH in DMF in an H-shaped divided cell revealed the formation of a new species in each electrode compartment as indicated by a change in the u.v. spectrum (Table 2). Extinction coefficients were calculated on the basis of single electron transfers when (I) is converted to (II) and (III) in the anode and cathode compartments, respectively.

Electrolysis in the absence of monomer at  $-60^\circ\text{C}$  for 1 h at 50 mA was effected and DPPH (0.2 g in 25 ml DMF) was added immediately the current was switched off. The u.v. spectrum indicated the presence of a species similar to that produced directly at the cathode (435 nm). This adsorption remained constant with time, indicating almost instantaneous electron transfer to DPPH, suggesting that anionic species were produced at the cathode and that their negative charge was transferred to the DPPH when the latter was added:



These reactions may be used to evaluate the rate constants,  $k_B$ ,  $k_C$  and  $k_D$  in the reaction scheme:



A simplified analysis of the results obtains if only the dimeric dianion  $(\text{DMF})_2^{2-}$  is assumed to react with the DPPH. As will be seen later both anionic species appear to react with DPPH.

The concentration of  $(\text{DMF})_2^{2-}$  may be obtained from the relationship:

$$(\text{DMF})_2^{2-} = \frac{I(1 - \exp(-k_B t))}{2FVk_B} \quad (13)$$

Substitution of the value of  $k_B$  obtained from the cyclic voltammetric data ( $2.32 \times 10^{-2} \text{ s}^{-1}$ ) indicates that  $(\text{DMF})_2^{2-}$  approaches a constant value after approximately 2 min electrolysis at 50 mA.

In order to determine  $k_C$  it was necessary to determine the decay of  $(\text{DMF})_2^{2-}$  after the current had been switched off, using the following reasoning. For simplicity,  $(\text{DMF})_2^{2-}$  is written as  $B$  and  $(\text{DMF})_2^{2-}$  as  $C$ :

$$\frac{-dB}{dt} = k_B B \quad (14)$$

$$B = B_0 \exp(-k_B t)$$

where

$$B_0 = I/2FVk_B$$

$$\begin{aligned}
 \frac{dC}{dt} &= k_B B - k_C C \\
 &= k_B B_0 \exp(-k_B t) - k_C C
 \end{aligned} \quad (15)$$

which may be written as:

$$\frac{dC}{dt} \exp(k_C t) + k_C C \exp(k_C t) = k_B B_0 \exp[(k_C - k_B)t] \quad (16)$$

Integration and evaluation of the integration constant gives:

$$C \exp(k_C t) - C_0 = \frac{k_B B_0}{k_C - k_B} (\exp(k_C - k_B)t - 1) \quad (17)$$

where  $C_0$  is the value of  $C$  when the current is switched off. Thus:

$$\exp(k_C t) = \frac{k_B B_0}{k_C - k_B} [\exp(k_C - k_B)t - 1] + \frac{C_0}{C} \quad (18)$$

This may be simplified if the time  $t$  is taken as the half-life  $t^{1/2}$  when  $C_0 = 2C$  and an approximate value of  $k_C$  can be obtained from  $\ln 2 = k_C t$ . Substitution of this value into the LHS of equation (18) enables a new value of  $k_C$  and hence  $C_0$  to be evaluated and by iteration through several cycles constant values of  $k_C$  and  $C_0$  can be obtained.

50 mA was passed for 1 h through a mixture of solvent and electrolyte at  $-60^\circ\text{C}$  to ensure that an equilibrium value of  $B$  was obtained. Following cessation of the current, samples were taken at regular intervals and the absorbance measured at 435 nm giving a decay curve as shown in Figure 2. The half-life is approximately 120 s, giving a value of  $k_C = 5.8 \times 10^{-3} \text{ s}^{-1}$  and  $B_0 = 1.12 \times 10^{-4} \text{ mol l}^{-1}$ .

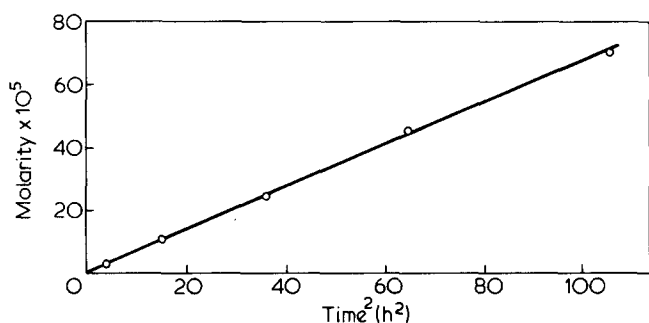


Figure 2 Production of glyoxal by the electrolysis of DMF containing 0.1 M  $(C_2H_5)_4NClO_4$

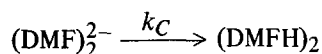
Values of  $C_0$  are obtained from a further integration:

$$C = \frac{I}{2FV} \left[ \frac{1}{k_C} - \frac{\exp(-k_B t)}{k_C - k_B} + \frac{\exp(-k_C t)}{k_C} - \frac{\exp(-k_C t)}{k_C - k_B} \right]$$

With  $t = 60$  min and  $k_C \cong 10^{-3} \text{ s}^{-1}$ , the last three terms of the equation become negligible and  $C_0$  can be readily calculated. Ten cycles showed that  $k_C = 8.12 \times 10^{-3} \text{ s}^{-1}$  and  $C_0 = 3.19 \times 10^{-4} \text{ mol l}^{-1}$ .

The theoretical half-life using this value of  $k_C$  becomes 85.3 s, so that the observed half-life (120 s) is approximately equal to the sum of the half lives of B and C. The poor agreement between the calculated value of  $C_0$  ( $3.19 \times 10^{-4} \text{ mol l}^{-1}$ ) and the observed value ( $4.45 \times 10^{-4} \text{ mol l}^{-1}$ ) may be resolved if it is considered that species B ( $DMF^{2-}$ ) reacts with the DPPH to give the  $DPPH^-$  anion, when the total theoretical effective concentration  $B_0 + C_0$  would be  $4.31 \times 10^{-4} \text{ mol l}^{-1}$  which is in good agreement with the observed value of  $4.45 \times 10^{-4} \text{ mol l}^{-1}$ .

Turning now to the reaction:



$$\frac{dD}{dt} = k_C C - k_D D$$

where  $D$  refers to  $[(DMFH)_2]$ . The rate of removal of  $(DMFH)_2$  to produce glyoxal and dimethylamine occurs with a rate constant  $k_D$ . Anticipating a low value of  $k_D$ :

$$-\frac{dD}{dt} = k_C C = 2.06 \text{ mol l}^{-1} \text{ s}^{-1}$$

after 10 min electrolysis when  $C$  becomes constant and  $dE/dt = k_D D$  where  $E$  is the concentration of glyoxal. Thus  $dE/dt = 2.06 \times 10^{-7} k_D t$ ; hence,  $E = 2.06 \times 10^{-7} k_D t^2$ . To a first approximation [glyoxal] and [dimethylamine] should have a square dependence on time.

During electrolysis of the solvent, electrolyte and DPPH, only an absorption occurred at  $\lambda_{\max} = 385 \text{ nm}$  ( $\epsilon = 2670$ ), this was ascribed to the presence of glyoxal<sup>11</sup>, dimethylamine being inactive in this region. When working at room temperature the absorption was linear with electrolysis time and the value of  $k_D$  was quite large. No increase in absorption occurred subsequent to termination of electrolysis. In order to work at  $-60^\circ\text{C}$  the reaction solution was pumped through a flow-through cell fitted in the u.v. spectrometer set to monitor at 295 nm and returned to the electrolysis

cell. The dead time for liquid to flow through the cell was about 2 s. At this low temperature,  $k_D$  was low and many hours of electrolysis were required before a reasonable plot of (glyoxal) versus (time)<sup>2</sup> could be made in order to obtain a value of  $k_D$  (Figure 2), using a calibration graph obtained at room temperature. The rate constant  $k_D$  is thus  $10^3$  smaller than either  $k_B$  or  $k_C$  even when the latter are expressed without the concentration term.

## CONCLUSION

It is apparent therefore that the electrochemical initiation of the polymerization of butyl isocyanate in the presence of DMF and quaternary ammonium salts is by no means simple. From cyclic voltammetry it would appear that butyl isocyanate undergoes a one electron reduction at a mercury cathode to form a radical anion which rapidly dimerizes to form the reduced dimer. This was confirmed by the isolation of the nickel complex of its dioxime derivative. The reduced dimer was found to be insufficiently basic to initiate polymerization. Pre-electrolysis of the solvent prior to monomer addition gave rise to a rapid polymerization reaction, because of the presence of a reduced form of the solvent which itself had a finite lifetime. Cyclic voltammetry indicates that a two electron reduction occurs producing a doubly charged anion, which, on condensation with a further molecule of dimethyl formamide, produces a symmetrical solvent-reduced dimer, analogous to the monomer species. It is not possible to state whether the doubly charged anion or the doubly charged reduced dimer is responsible for the initiation reaction. The solvent-reduced dimer appears to undergo a slow protonation reaction, eventually to decompose to glyoxal and dimethylamine; the glyoxal was determined as a nickel complex similar to that produced by the reduced dimer of butyl isocyanate. The source of protons giving rise to the protonation reaction is difficult to rationalize in terms of solvent which is normally considered to be aprotic. Similarly all experiments were carried out using techniques designed to reduce the presence of extraneous proton donors to a minimum. The inability to assign unequivocally the source of protons does not, however, detract from the more important hypothesis—that of the production of a reactive intermediate by the electrolysis of a solvent which is so often used as a vehicle for electrochemical reactions.

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