Anodic Oxidation of Alkyl Isocyanates and Their Thio Derivatives in Acetonitrile

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Seven alkyl isocyanates (RNCO), five alkyl isothiocyanates (RNCS), and two aromatic cyanato derivatives (ArNCO) were electrochemically investigated by cyclic voltammetry and anodic controlled-potential electrolysis in acetonitrile at platinum anodes. It was found that RNCS compounds exhibited considerably lower anodic potentials than RNCO derivatives. The preparative electrochemical oxidation of RNCS was dependent on the nature of the alkyl group. Primary RNCS afforded mainly five-membered heterocyclic products while tertiary ones gave largely amides due to α-cleavage or isocyanates due to substitution of sulfur for oxygen processes. RNCO compounds were oxidized at the onset of the solvent electrolyte region and yielded amides and carbonyl products due to nucleophilic involvement of either acetonitrile or water, respectively, or formed products due to radical reactions (mono-, di-, and tricyanomethyl derivatives). ArNCO gave mostly polymeric products. Mechanistic routes for the formation of the various products are discussed.

Most of our previous work on the anodic oxidation of cumulenes in nonaqueous media was focused on allenic hydrocarbons. In methanol[1] they behaved mostly as acetylenes by undergoing C=C and C—C bond cleavages to afford a wide spectrum of products. In acetonitrile[2] they behaved more selectively since in general they underwent oxidation only at one of the double bonds with retention of the second one. Our preliminary results on the anodic oxidation of heterocumulenes showed[3] a remarkable difference between them and the electrochemical behavior of allenic hydrocarbons. The former underwent mainly an α-cleavage process which was not observed in allenes.

In the present work we describe an extensive study on the anodic oxidation of both alkyl isocyanates (RNCO) and alkyl isothiocyanates (RNCS) in acetonitrile. In addition to π-bond oxidation and α-cleavage processes, a new electrochemical pathway for the formation of heterocyclic products has been discovered during the course of oxidation of primary alkyl isothiocyanates.

Results

Table I presents anodic peak potentials for alkyl isothiocyanates (**1a**–**1g**), alkyl isocyanates (**2a**–**2e**), and two aromatic cyanato derivatives (ArNCO) (**2f** and **2g**). Each of the anodic waves observed was found to be electrochemically irreversible. No reduction waves were observed in any voltammogram on reverse scans. Clearly, most RNCS derivatives afforded significantly lower oxidation potentials compared with those of the aliphatic RNCO. The latter derivatives were oxidized at ~3 V, whereas most RNCS (**1a**, **1b**, **1e**, and **1g**) oxidized at ~2 V. Compounds **1c** and **1d** showed, exceptionally, two oxidation waves at slow sweep rates.

Table II describes the wide spectrum of products obtained by the electrochemical oxidation of alkyl isothiocyanates. It seems that the type of products is highly dependent on the nature of the alkyl group attached to the cumulenic fuctionality. In general the primary alkyl isothiocyanates studied afforded five-membered-ring heterocyclic products consisting of either two molecules of the corresponding substrate (types **3** and **4**) or one molecule of a substrate and one molecule of acetonitrile (type **5**). All heterocyclic products have a carbonyl group in their structural formula and its source will be discussed later. Some primary substrates (**1c** and **1d**) yielded also noncyclic products (type **6**). However, tertiary alkyl isothiocyanates formed exclusively products of types **7** and **8**. Compound **1e** was the only one with a secondary alkyl group studied. This substrate gave only noncyclic products (**7a**, **8a**, and **9a**).

Table I. Anodic Peak Potentials for Organic Isocyanates and Isothiocyanates[a]

compd	R	E_p,[b] V
	in RNCS	
1a	Me	2.05
1b	Et	2.08
1c	*n*-Pr	2.62[c]
1d	*n*-Bu	2.28[d]
1e	cyclohexyl	2.07
1f	*t*-Bu	2.33
1g	1-adamantyl	2.05
	in RNCO	
2a	Et	3.18
2b	*n*-Pr	3.14
2c	*n*-Bu	3.20
2d	cyclohexyl	2.98
2e	*t*-Bu	3.06
2f	Ph	1.88
2g	2-naphthyl	1.27

[a] In CH_3CN–0.1 M $LiClO_4$ on Pt; sweep rate: 0.2 V/s for both forward and reverse scans, starting from and ending at 0 V. [Substrate] = 10 mM. All waves are electrochemically irreversible. [b] Vs. Ag/0.1 N $AgNO_3$ reference electrode (0.32 vs. SCE). [c] At 20 mV/s this wave separates into two, E_p^1 = 2.25 V and E_p^2 = 2.62 V. [d] As in footnote c; E_p^1 = 2.10 V and E_p^2 = 2.30 V.

Table III complements Table II by presenting electrochemical data (oxidation potentials used in preparative electrolysis and amount of electricity consumed in each electrolysis) and other data (concentrations, type of products formed, and relative yields). In the case of **1a** and **1b** it was found that the ratio between type **3** products and type **4** products was affected by varying the anodic applied potential (entries 1 vs. 2 and entries 5 vs. 6). Furthermore, the sum yield of **3** + **4** decreases with increasing electricity consumption (entries 3 vs. 1 and 2 and entries 7 vs. 5 and 6). As to **1c**–**1e**, about 50% of the starting material is left even after ~2 F/mol (entries 8,

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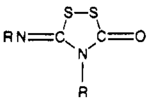
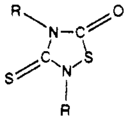
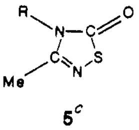
(1) Becker, J. Y.; Zinger, B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 395. Becker, J. Y. *Isr. J. Chem.* **1985**, *25*, 196.

(2) Becker, J. Y.; zinger, B. *Tetrahedron* **1982**, *38*, 1677. *Electrochim. Acta* **1980**, *25*, 791.

(3) Becker, J. Y.; Zinger, B. *J. Am. Chem. Soc.* **1982**, *104*, 2327.

0022-3263/87/1952-2783$01.50/0

Table II. Electrolysis Products by Anodic Oxidation of RNCS in CH_3CN

assignment	R	structural formula
3a **3b** **3c** **3d**	Me Et *n*-Pr *n*-Bu	 **3**[a]
4a **4b** **4c** **4d**	Me Et *n*-Pr *n*-Bu	 **4**[b]
5a **5b** **5c**	Et *n*-Pr *n*-Bu	 **5**[c]
6a **6b**	*n*-Pr *n*-Bu	RNHCONHR (**6**)
7a **7b**	cyclohexyl 1-adamantyl	RNCO (**7**)
8a **8b** **8c**	cyclohexyl *t*-Bu 1-adamantyl	$RNHCOCH_3$ (**8**)
9a	cyclohexyl	RNHCHO (**9**)

[a] 4-Alkyl-5-(alkylimino)-1,2,4-dithiazolidine-3-one. [b] 2,4-Dialkyl-1,2,4-thiadiazolidine-3-thione-5-one. [c] 3-Methyl-4-alkyl-1,2,4-thiadiazolidine-2-ene-5-one.

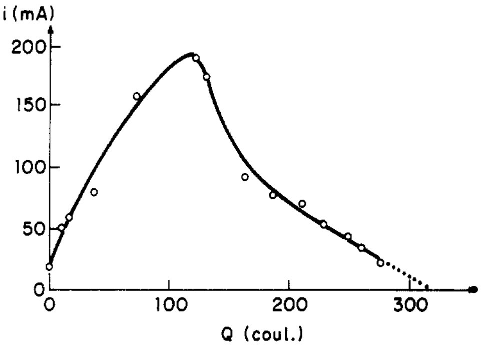


Figure 1. Current–charge curve for **1a** (entry 1, Table III). For $n = 1$ F/mol, the electricity consumption is 315 C.

12, and 16) is consumed. When the electricity consumption was increased (entries 7, 10, and 14), a complicated products mixture was achieved in which none of the products was identified. Products due to α-cleavage or substitution (sulfur for oxygen) processes were formed only by the oxidation of **1e**–**1g** (entries 15–23). Substrate **1e** was chosen to be studied under various experimental conditions, e.g., in divided and nondivided cells (entries 15 and 18, respectively), and in the presence of 1% H_2O in divided and nondivided cells (entries 16 and 17, respectively).

Table IV contains details on electrolyses of alkyl isocyanates and describes both electrochemical experimental conditions and products. Most products derived from primary alkyl isocyanates contained at least one nitrile group, whereas those derived from secondary or tertiary alkyl groups contained mostly carbonyl and/or acetamido functionalities. The two aromatic isocyanates studied behaved entirely different, as evidenced by the type of products they formed, mainly because they are oxidized at significantly lower potentials than those of the alkyl isocyanates.

Table III. Results of Preparative Electrolysis of RNCS in CH_3CN–0.1 M $LiClO_4$

entry	substrate (mM)	*E*, V	F/mol	products (%)[b]
1	**1a** (120)	2.1	0.8	**3a** (22); **4a** (78)
2	**1a** (136)	2.25	0.8	**3a** (40); **4a** (60)
3	**1a** (120)	2.1	2.0	**3a** (25); **4a** (50)
4	**1a** (170) + **2a** (170)	2.2	1.0	results similar to those of entry 2
5	**1b** (100)	1.8	1.0	**3b** (43); **4b** (51); **5a** (5)
6	**1b** (120)	2.1	0.9	**3b** (72); **4b** (19); **5a** (9)
7	**1b** (171)	2.4	1.9	*c*
8	**1c** (77)	2.4	2.0	**1c** (52); **3c** (11); **4c** (10); **5b** (10)
9	**1c** (128)	2.4	2.9	**3c** (33);[d] **4c** (67);[d] **6a** (23)[e]
10	**1c** (80)	2.4	5.4	*c*
11	**1d** (68)	2.4	1.0	**1d** (90); **4d** (10)
12	**1d** (68)	2.4	2.0	**1d** (41); **3d** (25); **4d** (3); **5c** (11)
13	**1d** (68)	2.2	2.9	**1d** (9); **3d** (41); **4d** (14); **5c** (14)
14	**1d** (68)	2.4	5.5	*c*
15	**1e** (94)	2.25	1.0	**1e** (34); **7a** (26); **8a** (40)
16	**1e** (118) + 1% H_2O	2.35	2.0	**1e** (55); **7a** (34); **8a** (11)
17	**1e**[f] (113) + 1% H_2O	2.25	5.0	**1e** (9); **7a** (30); **9a** (37)[g]
18	**1e** (117)	2.45	5.0	**1e** (40); **7a** (5); **9a** (48)[g]
19	**1f** (66)	2.25	1.0	**8b** (86)
20	**1f** (64)	2.25	2.0	**8b** (83)
21	**1f** (65)	2.25	3.0	**8b** (76)
22	**1g** (87)	2.2	1.2	**7b** (2); **8c** (94)
23	**1g**[f] (87)	2.2	2.2	**1g** (42); **7b** (20); **8c** (32)

[a] All electrolyses were carried out in an H type cell divided by medium glass frit, unless otherwise noted. All potentials are quoted vs. Ag wire quasi-reference electrode (+0.39 V vs. NHE). [b] % refers to relative ratio determined by GLC or ^1H NMR integration. Total yield based on weight of isolated product mixture relative to the amount of reacting substrate. It ranges between 30 and 50% for primary RNCS and 60 and 80% for tertiary ones. Each reaction yielded 2–4 additional unidentified products. [c] Unidentified complex mixture. [d] These isomers precipitate upon workup. [e] Product **6a** was found in the liquid phase from which **3c** and **4c** were precipitated. This phase contained three additional unidentified products. [f] Electrolyses were carried out in a nondivided cell. [g] Electrolyses of either **1a** or **1b** under similar conditions did not yield MeNHCHO or EtNHCHO, respectively. It seems that polymerization took place at the cathode in each one of these cases.

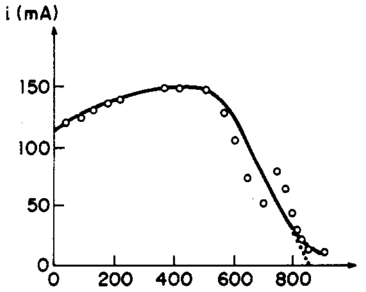


Figure 2. Current–charge curve for **1c** (entry 8, Table III). For $n = 1$ F/mol, the electricity consumption is 331 C.

Table V describes ^1H NMR, IR, and MS data of the products obtained from both alkyl isocyanates and alkyl isothiocyanates. The ratio $(M + 2)/M$ in the MS confirms nicely the existence of one or two sulfur atoms in each of the products of type **3**, **4**, and **5**.

Table IV. Results of Preparative Electrolysis of RNCO[a]

entry	compd (M)	E, V[b]	F/mol[c]	cell[d]	products (%)[e]	no. of unidentified products (%)
1	**2a** (0.19)	2.80	1.1	ND[f]	**10**, $MeCH(CH_2CN)_2$ (100%)	–
2	**2b** (0.13)	2.75	1.0	ND[f]	**11**, n-$PrCH_2CN$ (40) **12**, Me_2CHCH_2CN (60)	*g*
3	**2c** (0.14)	2.75	1.0	ND	**13**, $Me(CH_2)_2COOH$ (67) **14**, $MeCH_2CH(CH_2CN)CH_2OH$ (25)	3 (8)
4	**2c** (0.17)	2.75	0.9	D[f]	**15**, $MeCH_2CH(CN)C(CH_2CN)_3$ (86)	3 (14)
5	**2d** (0.11)	2.90	0.8	ND	**16**, cyclohexanone (18) + **2d** (75)	2 (7)
6	**2d** (0.10)	2.80	1.0	D	**17**, *N*-cyclohexylacetamide (3) + **2d** (89)	2 (8)
7	**2d** (0.13)	2.80	0.4	ND + 1% H_2O	**18**, $C_6H_{13}NHCONHC_6H_{13}$ (36)[h]	
8	**2e** (0.11)	2.75	1.0	ND	**8a**, $(Me)_3CNHCOCH_3$ (67) **19**, $Me_3CNHCOCH_2CN$ 14)	2 (19)
9	**2e** (0.21)	3.22	0.9	D	**19** (48) **20**, Me_3CCN (15)	7 (37)
10	**2f** (0.12)	1.9	0.9–1.2	D or ND	solid (polymer)[i]	
	2g (0.11)	1.3	0.7	D	solid (polymer)[i,j]	

[a] In HPLC grade CH_3CN–0.1 M TEAF on Pt anode. [b] Oxidation potentials vs. Ag/0.1 N $AgNO_3$. [c] Faraday (per mol) consumed by the end of electrolysis when current reached the value of background. Values of F/mol were corrected for background currents assuming the latter constant throughout electrolysis. [d] D = a divided cell in which anode and cathode compartments were separated by medium glass frit; ND = nondivided cell, a beaker. [e] Relative yields were estimated by GLC integration. [f] CH_3CN was dried over activated alumina for 24 h before electrolysis. [g] A trace amount of a carboxylic acid was detected by ^1H NMR. [h] This is a chemical yield based on isolated product relative to initial amount of substrate. [i] $LiClO_4$ was used as electrolyte. A solid precipitates out during electrolysis. It decomposes before it melts. It is soluble in Me_2SO. [j] α-Aminonaphthalene (**21**) was also detected. It could be generated by a nonelectrochemical product formed by direct hydrolysis of the highly reactive **2g** followed by instantaneous decarboxylation.

Two typical representative examples of current–charge curves (coulometric experiments) are given by Figures 1 and 2 for substrates **1a** and **1c**, respectively. No similar figures for RNCO derivatives were available due to their high oxidation potential under which high background currents masked the faradaic ones.

Discussion

As is evidenced by the electrochemical data presented in Table I, alkyl isothiocyanates (**1a**–**1g**) are oxidized at considerably lower positive potentials than alkyl isocyanates (**2a**–**2e**). Since the only difference between these two families of compounds lies in the structure of their corresponding terminal double bonds, namely, C=S vs. C=O, this must be the reason for the marked shift in their corresponding oxidation potentials. A reasonable explanation for this difference is based on the composition of the HOMO in each system. In allenes it involves exclusively the π electrons of the double bonds, while in heterocumulenes it may involve also lone pair(s) of heteroatom(s). Our initial MO computations[4] for RNCO and RNCS (R = H and Me) support this hypothesis; the lone pair of sulfur is involved in the HOMO of RNCS, and the lone pair of nitrogen is involved in the HOMO of both RNCS and RNCO. A further support stems from photoelectron spectroscopy measurements,[5] which afford 9.94 and 9.37 eV for HNCS and MeNCS, respectively, compared with 11.62 and 10.67 eV for HNCO and MeNCO, respectively.

It seems that for all aliphatic RNCO and for most aliphatic RNCS (**1a**, **1b**, **1e**, and **1g**) the anodic potentials are almost insensitive to the extent of inductive effect exerted by the alkyl group attached to the cumulenic functionality. However, steric effects may be more important in affecting anodic potentials, as can be seen for either *tert*-butyl derivative, **1f** (with respect to **1a**, **1b**, and **1g**) or **2e** (with respect to **2a**–**2d**), thus each possesses a higher anodic potential than is anticipated by a pure inductive effect consideration. This issue was discussed in detail for RNCS derivatives elsewhere.[6]

It is not surprising that each of the two aromatic isocyanates studied (**2f** and **2g** in Table I) had a significantly lower oxidation potential than the aliphatic ones. Obviously the aromatic π system has a major contribution to the HOMO of **2f** or **2g**. This assumption is supported by the observation[7] that the anodic oxidation potentials of benzene and naphthalene are 2.08 and 1.34 V, respectively, similar to the values of their corresponding isocyanates.

A. Isothiocyanates. Table II, which lists a variety of products obtained from **1a**–**1g**, also indicates the dramatic change in type of products yielded by primary alkyl isothiocyanates compared with those derived from tertiary ones. Apparently, the formation of three different types of heterocyclic five-membered rings is favored by the anodic oxidation of primary **1a**–**1d** derivatives. In contrast, the anodic oxidation of secondary (**1e**) and tertiary (**1f** and **1g**) RNCS led preferentially to α-cleavage products (type **8**) and to the formation of RNCO derivatives (type **7**). It is not surprising that an α-cleavage process takes place exclusively in secondary and tertiary RNCS because they could form relatively stable carbocations in acetonitrile. In fact, this process is also predominant in the oxidation of tertiary **1f** and **1g** (entries 19–23, Table III). However, when the carbocation intermediates are unstable, as in primary RNCS, an alternative route is favored, as is evidenced by the heterocyclic products formed. As to the formation of RNCO products from RNCS, oxidation of the C=S bond is to be expected since the HOMO in RNCS involves also the lone pair of the sulfur atom.[4] Surprisingly, this process does not take place at all in the case of primary RNCS, presumably because the formation of heterocyclic products is much faster. It is noteworthy that a similar chemical process (eq 1), in which oxygen is substituted by sulfur atom takes place in the 1,3-dipolar cycloaddition of isothiocyanates:[8]

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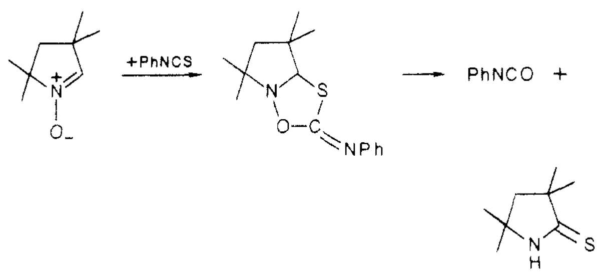
[4] Zinger, B. Ph.D. Dissertation, Ben-Gurion University, 1981 (STO-3G, open-shell MO computations).

[5] Cradock, S.; Ebsworth, E. A. V.; Murdoch, J. D. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 86.

[6] Becker, J. Y.; Zinger, B. *J. Electroanal. Chem.* **1984**, *176*, 203.

[7] Loveland, J. W.; Dimler, J. R. *Anal. Chem.* **1969**, *33*, 1196.

[8] Black, D. St. C.; Watson, K. G. *Tetrahedron Lett.* **1972**, 4191.



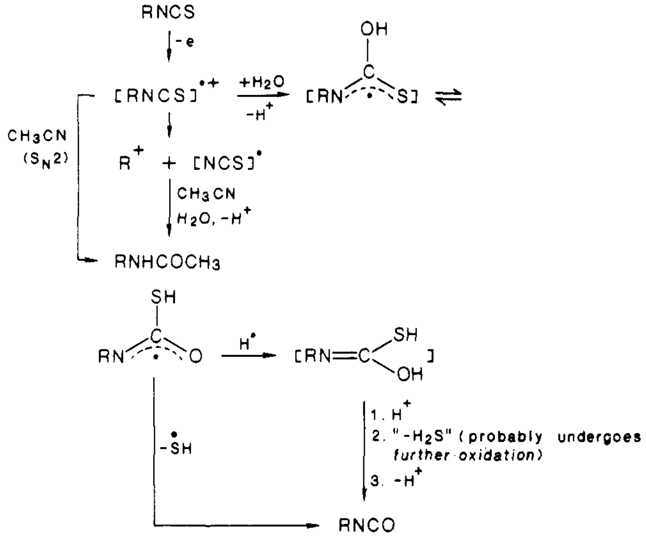
(1)

An interesting point is the change in ratio between the amide **7a** and the isocyanate **8a** when electrolysis of **1e** took place under various experimental conditions. Addition of water to the electrolyte (entries 15 and 16 in Table III) decreases the current efficiency, because although more electricity was consumed, less starting material was reacted. This is probably due to a competing water oxidation reaction with that of the substrate. However, the presence of water slightly increased the yield of **7a** but sharply decreased that of **8a**. It is probable that under "wet" conditions, hydroxide ions could be formed in the cathode compartment and diffuse to the anodic one. Since they are better nucleophiles[9] than H_2O, they facilitate the formation of RNCO. Interestingly, comparison of the experiments in the one-compartment cell (entries 17 and 18) indicates that the presence of water does not seem to compete with the oxidation of the substrate but to improve the relative yield of **7a** (30% vs. 5%). Also, two other noteworthy points were observed: (a) no **8a** was formed in the one-compartment cell, neither in the divided nor in the one-compartment cell; (b) a new type of product, **9a**, was detected, which is believed to be formed by the reduction of **7a** at the cathode.

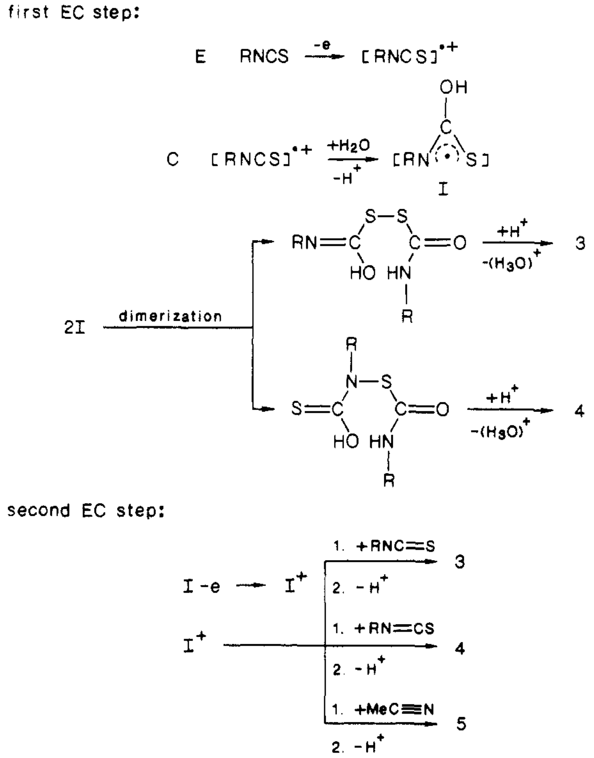
Scheme I describes a possible mechanism for the formation of RNCO and $RNHCOCH_3$ products from secondary and tertiary RNCS. The initial electrochemical process generates a cation radical which may either undergo α-cleavage to form acetamido derivatives (via S_N1 type mechanism) or react with acetonitrile or water to form $RNHCOCH_3$ (via S_N2 mechanism) and RNCO products, respectively. Although the S_N2 type mechanism for the formation of $RNHCOCH_3$ from $[RNCS]^{\bullet +}$ cannot be entirely excluded, it is disfavored since no amides were formed from *primary* RNCS (entries 1–13, Table III). This observation may point to an S_N1 type mechanism for the formation of amides.

The lack of stability of primary carbocations promotes the formation of heterocycles **3**, **4**, and **5** (Table II) from **1a**–**1d**. However, the electrochemical properties and product distribution are different within the primary RNCS themselves. For instance, **1a** and **1b** are oxidized at lower potentials than **1c** and **1d** (Table I). Furthermore, only **1c** and **1d** exhibit two distinctive oxidation waves in their cyclic voltammograms. Controlled-potential electrolysis of **1a** or **1b** was usually terminated after consuming ~1 F/mol when all the starting material was consumed and the current usually reached its background value (Figure 1 and entries 1–7, Table III). However, substrates **1c** and **1d** were still present in the product mixture even after 2–3 F/mol was consumed (Figure 2 and entries 8–13, Table III). To add to the complexity, a product of type **5** (Table II) was not formed from **1a**, while product type **6** was formed only from **1c** and **1d** (Table II). Also, in either Figure 1 or 2 the current does not decay exponentially but forms a "hump", which may indicate the existence of electrochemically active intermediates (e.g., I in Scheme II) that compete favorably with the oxidation of the substrate. Evidently not all reactive intermediates led to products that could be fully characterized. This made us believe that polymerization took place, too, hence the relatively low chemical yield especially from primary and secondary RNCS (Table III). It would be very difficult to rationalize all the above discrepancies in one mechanistic scheme; however, we suggest a plausible EC (electrochemical-chemical) type mechanism which could explain the formation of the cyclic products type **3** and **4** from **1a** and **1b** by 1-electron oxidation and an ECEC mechanism for the formation of **3**–**5** (e.g., from **1c** and **1d**, Table II) by 2-electron oxidation. Scheme II describes just a few and oversimplified routes that may take place after the initial electron transfer to electrogenerate $[RNCS]^{\bullet +}$. Obviously the latter could react not only with H_2O (in analogy with the nucleophilic reaction of RNCS with amines[10]) as described in Scheme II but also with other

Scheme I



Scheme II



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[9] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1976; pp 187–191.

Table V. Spectroscopic Data of Products

	^{1}H NMR (δ)	IR, cm^{-1}	MS (*m/e*, %)
3a	3.14 (s); 3.26 (s)	1705 (C=O); 1640 (C=N)	EI: 162 (M$^+$, 28,); 105 (73); 69 (100); 64 (51) CI: 162 (M$^+$)
3b[a]	1.23 (t); 1.28 (t); 3.35 (q); 3.89 (q)	1695; 1620	EI: 190 (M$^+$, 38); 119 (100); 91 (53); 83 (65); 69 (32)
3c	1.00 (t, t); 1.7–1.9 (m); 3.25 (t); 3.81 (t)	1690; 1630	EI: 218 (M$^+$, 17); 133 (25); 76 (40); 55 (52); 43 (100)
3d	0.96 (t, t); 1.25–1.85 (m); 3.23 (t); 3.83 (t)	1670; 1630	EI: 246 (M$^+$, 13); 190 (28); 147 (20); 57 (100) CI: 247 (M + 1)
4a[b]	3.45 (s); 3.55 (s)	1705	EI: 162 (M$^+$, 100); 74 (55); 69 (37); 61 (32)
4b[c]	1.32 (t); 1.37 (t); 4.13 (q); 4.16 (q)	1705	EI: 190 (M$^+$, 92); 97 (100); 88 (23); 69 (68); 60 (36)
4c	1.0 (t, t); 1.65–1.9 (m); 4.01 (q); 4.05 (q)	1700	EI: 218 (M$^+$, 74); 176 (40); 55 (52); 43 (100); 133 (25)
4d	0.96 (m); 1.25–1.85 (m); 4.05 (q); 4.08 (q)	1690	CI: 247 (M + 1)
5a[d]	1.31 (t, 3 H); 2.38 (s, 3 H); 3.80 (q, 2 H)	1672	EI: 144 (M$^+$, 100); 103 (14); 74 (13)
5b[d]	0.98 (t); 1.70 (m); 2.35 (s); 3.69 (t)	1675	EI: 144 (M – 14, 11); 97 (36); 85 (22); 71 (42); 69 (41) CI: 159 (M + 1)
5c[d]	0.97 (t); 1.3–1.7 (m); 2.36 (s); 3.70 (t)	1680	EI: 172 (M$^+$, 16); 116 (17); 98 (59); 73 (100)
6a[e]	0.93 (t); 1.4–1.7 (m); 3.13 (t); 5.60 (br, 1 H)	3430; 1660	EI: 144 (M$^+$, 74); 115 (18); 87 (10); 73 (18); 60 (18); 58 (100); CI: 145 (M + 1)
6b	0.93 (t); 1.2–1.6 (m); 3.20 (t)		EI: 115 (M$^+$, 15); 69 (46); 57 (100) CI: 173 (M + 1)
7a	1.1–2.0 (m, 10 H); 3.4 (m, 1 H)	2270	EI: 125 (M$^+$, 7); 97 (18); 83 (70); 67 (100)
7b	1.65 (m, 6 H); 1.9 (m, 3 H); 2.15 (s, 6 H)	2305	
8a	1.1–2.0 (m, 10 H); 1.92 (s, 3 H); 3.7 (s, 1 H); 5.3 (br, 1 H)	1660	EI: 142 (M + 1, 86); 98 (22); 60 (96); 56 (100); 43 (82) CI: 141 (M$^+$)
8b	1.34 (s, 9 H); 1.92 (s, 3 H); 5.30 (br, 1 H)	1655; 3360	EI: 115 (M$^+$, 9); 100 (37); 58 (100); 43 (31)
8c	1.69 (t, 6 H, *J* = 2 Hz); 1.89 (s, 3 H); 2.02 (s, 9 H); 5.25 (br, 1 H)	3300; 1660	
9a	1.1–2.0 (m, 10 H); 3.76 (m, 1 H); 6.54 (br, 1 H); 7.9 (s, 1 H)	3280; 1660	EI: 128 (M + 1, 100); 84 (28); 56 (74) CI: 127 (M$^+$)
10	1.28 (d, 3 H, *J* = 7 Hz); 2.46 (d, 4 H, *J* = 7 Hz); 2.45 (m, 1 H)	2270	EI: 68 (100); 52 (13) CI: 108 (M$^+$)
11	1.08 (d, 6 H, *J* = 6); 2.0–2.6 (m, 6 H)	2350	CI: 83 (M$^+$)
12	0.92 (t, 3 H, *J* = 8 Hz); 2.0–2.6 (m, 6 H)	2350	EI: 82 (M – 1, 68); 55 (100); 54 (52)
13	0.94 (t, 3 H, *J* = 6 Hz); 1.67 (m, 2 H); 2.32 (t, 2 H, *J* = 7 Hz), 10.16 (s, 1 H)	3370; 1730	EI: 88 (M$^+$, 3); 73 (30); 60 (100); 45 (17)
14	0.94 (t, 3 H, *J* = 7 Hz); 1.52 (m, 3 H); 2.51 (d, 2 H, *J* = 6); 2.96 (s, 1 H); 3.92 (t, 2 H, *J* = 6 Hz)	3350; 2310	EI: 73 (18); 55 (100) CI: 113 (M$^+$)
15	1.07 (t, 3 H, *J* = 7 Hz); 1.74 (m, 2 H); 2.76 (s, 6 H); 2.98 (m, 1 H)	2300	EI: 200 (M$^+$, 31); 199 (10); 184 (81); 171 (98)
19	1.37 (s, 9 H); 3.27 (s, 2 H); 4.53 (br, 1 H)	2280; 1660	EI: 140 (M$^+$, 3); 125 (25); 85 (7); 57 (100); 40 (6)
20	1.54 (s)	2320	EI: 84 (M + 1, 100); 56 (21) CI: 83 (M$^+$)
21	6.64 (m, 1 H); 7.22 (m, 2 H); 7.37 (m, 2 H); 7.68 (m, 2 H)	3300; 1660	EI: 143 (M$^+$, 100); 115 (62)
3b·HClO$_4$	1.32 (t, 3 H); 1.45 (t, 3 H); 3.85 (q, 2 H); 4.17 (q, 2 H); 10.0 (br s, 1 H)	*f*	

[a] Yellow liquid. Calcd for $C_6H_{10}N_2OS_2$: C, 37.89; H, 5.26. Found: C, 38.11; H, 5.42. [b] White solid, mp 103 °C. Calcd for $C_4H_6N_2OS_2$: C, 29.60; H, 3.70. Found: C, 29.35; H, 3.81. [c] White solid, mp 43–44 °C (compared with 45 °C in ref 17). Calcd for $C_6H_{10}N_2OS_2$: C, 37.89; H, 5.26; S, 33.60. Found: C, 37.77; H, 5.27; S, 33.62. [d] Data are in agreement with ref 12. [e] Data are in agreement with ref 18. [f] The salt exhibited a typical UV absorption for S–S bond at λ_{max} = 260 nm (ϵ = 600).[19]

nucleophiles such as CH_3CN, RN=CS, or RNC=S to yield the final products. Although these possibilities are not described in Scheme II, they certainly cannot be excluded.

Each of the cyclic products **3–5** contains a carbonyl group. The source of oxygen does not stem from atmospheric oxygen or perchlorate since the same results were obtained when electrolysis was carried out under nitrogen and in the presence of Et_4NBF_4 (TEAF) as electrolyte. This leaves the alternative possibility that its source stems from water contamination in acetonitrile (we used HPLC grade without further purification) or electrolyte or both.

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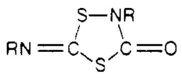
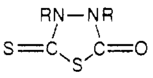
We also know that RNCO is not an intermediate in the cyclization process since when **1a** was electrolyzed in the presence of **2a** (entry 4 in Table III) similar results to those without the presence of **2a** were obtained.

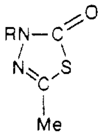
The dimerization of intermediates I in Scheme II could have led to other heterocyclic derivatives containing carbonyl groups **3′–5′**; which are isomers of **3–5**, respectively.



3′



4′



5′

We were able to eliminate structures **3′–5′** by comparison of their spectral data with those published for some of the chemically made derivatives of types **3–4**[11] (by Br_2 oxidation of RNCS) and **5**.[12a] For instance, the ^{1}H NMR results of **5a** were in excellent agreement (±0.02 ppm) with those published in ref 12a for the same compound, whereas there is a significant difference between the chemical shifts of the $N-CH_3$ groups in **5** and **5′** (3.32 and 3.52 ppm, respectively).[12] Additional supportive observations to the suggested structural assignments are as follows: (a) Product **3b** occasionally precipitated as its salt, **3b**·$HClO_4$, after workup. Unfortunately, the crystals showed a disordered structure with *R* factor of ~15%. However, the crude X-ray structure results confirm the basic suggested structure for **3b** and also show that in the solid state of the salt the ethyl group attached to the imino nitrogen is syn to the S–S bond of the five-membered heterocyclic ring. (b) The above-mentioned salt shows a UV absorption at λ_{max} = 260 nm, which is characteristic of a S–S bond (see footnote "f" in Table V). (c) Our recent results on the thermal behavior of compounds of type **3** indicate that the latter undergo isomerization (to products of type **4**) and decomposition to form carbodiimides (RN=C=NR) by two competitive routes. The ratio between the two types of products depends both on the nature of the R group in **3** and on the temperature (a detailed report on these results will be published later). Clearly, both types of products afford a further support to the suggested molecular structures of the heterocyclic products.

Products of type **6** (Table II) that were achieved only from the oxidation of **1c** and **1d** could be formed chemically from an intermediate product (eq 2) and RNCO as follows:

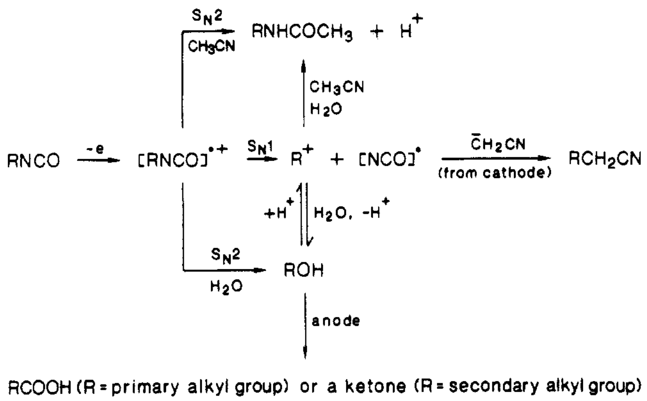
$$\mathrm{RNCO} \xrightarrow{H_2O} [\mathrm{RNHCOOH}] \xrightarrow{-CO_2} \mathrm{RNH_2} \qquad (2)$$

$$\mathrm{RNCO} + \mathrm{RNH_2} \rightarrow \mathbf{6}$$

B. Isocyanates. Each of the alkyl isocyanates studied (**2a–2e**, Table I) has a high anodic potential, well into the onset of the solvent–electrolyte region. Therefore, it is not surprising that preparative electrolysis in this region may lead to polymeric products that lower both products and current yields as well as form complex product mixtures due to participation, e.g., of the solvent. Electricity consumption was particularly low, and in quite a few cases it did not exceed even 1 F/mol, possibly due to a surface blockage by insulating polymeric film.[13]

From Table IV it is clear that four main types of products are achieved by oxidation of aliphatic RNCO: (1) products that involve water (which is present as contaminant in the solvent or electrolyte or both) acting as a nucleophile and displacing the NCO group to afford alcohol, ketone, or acid derivatives as the final products (e.g., **13**, **14**, and **16**); (2) products that stem from the involvement of acetonitrile as a nucleophile displacing the NCO group to yield acetamido derivatives (e.g., **8a**, **17**, and **18**); (3) a process involving acetonitrile via a homolytic process to generate products with one (e.g., **11** and **12**) or more (e.g., **10** and **15**) CH_2CN groups; (4) products containing a CN group, presumably formed by cyanation (e.g., **15** and **20**) reaction (vide infra).

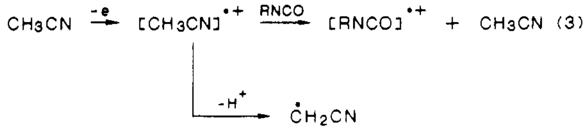
Scheme III



Clearly most acetamido derivatives were formed from secondary and tertiary RNCO, whereas products that included oxygen from water were generated by the oxidation of primary RNCO. It is noteworthy that products containing one CH_2CN group or more were formed only when an especially dry acetonitrile was used, as indicated by footnote *f* in Table IV. Obviously it is expected that under these conditions no products resulting from water involvement would be formed.

Substrate **2d** was studied under three different experimental conditions (entries 5–7, Table IV). In either divided (entry 6) or nondivided (entry 5) cells the yield was poor and most of the substrate remained unchanged. Each experiment yielded entirely different types of products. While amide **17** was observed in a divided cell, the ketone **16** was formed in nondivided cells in which hydroxide ions could be formed at the cathode and compete favorably with acetonitrile as a nucleophile. In the presence of water (entry 7), hydrolysis of **2d** took place to afford the urea derivative **18**. In the oxidation of **2e** (entry 8), no alcohol was observed; even if it would form, it could be easily protonated to give a stable carbocation which then further reacts with acetonitrile irreversibly (Scheme III). Surprisingly, no amide **8a** was detected in the product mixture of the divided-cell experiment (entry 9). Instead, two new products were achieved (**19** and **20**), which will be discussed later.

Considering the high anodic working potential of aliphatic isocyanates, the mechanism for products formation could be either direct or indirect; i.e., the substrate could be directly oxidized at the anode to form its radical cation, $[RNCO]^+$, followed by subsequent chemical reactions or the oxidation of CH_3CN (eq 3) forms an active species which then initiates the oxidation of the substrate:



$$\mathrm{CH_3CN} \xrightarrow{-e} [\mathrm{CH_3CN}]^{\cdot+} \xrightarrow{RNCO} [\mathrm{RNCO}]^{\cdot+} + \mathrm{CH_3CN} \quad (3)$$
$$[\mathrm{CH_3CN}]^{\cdot+} \xrightarrow{-H^+} \dot{\mathrm{C}}\mathrm{H_2CN}$$

Neither of the mechanisms could be excluded, although

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[11] Parmjpe, M. G.; Gosair, R. K. *Indian J. Chem.* **1967**, *5*, 125. Bambas, L. L. In *The Chemistry of Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience: New York, 1952; Vol. 4, Chapter 2.

[12] (a) Sumengen, D.; Pleter, A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 68. (b) Kristinsson, K.; Winkler, T. *Helv. Chim. Acta* **1982**, *65*, 2606.

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the fact that the current increased upon addition of a substrate (as indicated both by cyclic voltammetry and preparative electrolysis) supports the direct mechanism. Scheme III outlines some of the possibilities for products formation by a nucleophilic displacement type mechanism. Certainly it does not describe the formation of all the products listed in Table IV. A homolytic type mechanism for those products that contain CH_2CN or CN groups cannot be excluded.

Both **15** and **20** have a cyano (not a CH_2CN) group, which may indicate that a cyanation process takes place. Although we have no direct evidence for it, we do have a working hypothesis. It is well established[14] that $[NCO]^-$ undergoes anodic oxidation (eq 4) to form a dimer which then decomposes to cyanogen and molecular oxygen. This process is catalyzed by platinum anode:

$$[NCO]^- \rightarrow [NCO]^\bullet \rightarrow (NCO)_2 \rightarrow (CN)_2 + O_2\uparrow \qquad (4)$$

In our case, if $[RNCO]^{\bullet+}$ undergoes α-cleavage to form a carbocation and $[NCO]^\bullet$, then cyanogen could be formed in the manner described above. Apparently, products **15** and **20** may be indirect evidence for the cyanogen presence. (The cyanation process could be either heterolytic or homolytic).

As to the conjugated aromatic isocyanates derivatives (**2f** and **2g** in Table IV), each one of them has a considerably lower oxidation potential relative to that for alkyl isocyanates, presumably because their corresponding HOMO's contain mainly the aromatic π-electrons. Preparative electrolysis of either of them in a divided or nondivided cell afforded solids which precipitated out during electrolysis. We assume these are polymers that may be initiated also at the cathode.[15] (The electrolyses of **2f** and **2g** were conducted in the presence of $LiClO_4$ and not a tetraalkylammonium salt because the latter is known to catalyze their polymerization.[16])

Experimental Section

Materials. All substrates in this study were commercially available (Aldrich) and used without further purification. Acetonitrile was HPLC grade (from Fisons) or analytical grade (from Fisher). Only the latter was refluxed for 5 h over P_2O_5 and then distilled before use. Tetraethylammonium tetrafluoroborate was electrochemical grade, purchased from Southwestern Analytical Chemicals. Tetrabutylammonium perchlorate (Fluka) and lithium perchlorate (Alfa) were also used without further purification.

Cyclic Voltammetry Measurements. Princeton Applied Research potentiostat Model 173 and Universal programmer Model 175 were used along with a Yokogawa *xy* recorder Model 3036. The electrochemical cell was described elsewhere.[1,2] All potentials were recorded vs. a Ag/0.1 M $AgNO_3$ reference electrode at a platinum disk electrode (3.0×10^{-3} cm^2).

Controlled Potential Electrolysis. An H type cell was used for bulk electrolyses.[1,2] Isocyanates were oxidized at potentials quoted vs. Ag/0.1 M $AgNO_3$ (+0.56 V vs. NHE) and alkyl isothiocyanates vs. Ag wire (+0.39 V vs. NHE) reference electrodes. In all cases platinum anodes and stainless steel auxiliary cathodes were used. Electrolysis was usually terminated when the current reached its background value or arbitrarily stopped after a predetermined amount of electricity was consumed. In certain cases when current dropped quickly, continuous pulsing to 0 V every 5 s was necessary in order to maintain a reasonable current. The number of coulombs consumed was measured by a homemade integrator totalizer.

Workup. At the end of each electrolysis, the solvent was evaporated until 3–5 mL was left, followed by addition of water. When $LiClO_4$ was used as electrolyte, the solution was extracted into CH_2Cl_2, separated from water (the aqueous phase was always acidic), dried over $MgSO_4$, and filtered. When tetraethylammonium tetrafluoroborate was used, the solution was extracted into diethyl ether by the same procedure, washed twice with water, and followed by preparative GLC separation (SE–30 10% on Chromosorb W, 2 m × $^1/_4$ in.) and NMR, IR, and MS measurements. It should be pointed out that the separation between products of types **3** and **4** was difficult even though different columns were tried. The resolution of peaks was extremely sensitive to column conditions. Sometimes two distinct peaks were observed, and sometimes they merged into one. The reason for this kind of behavior has not been clarified yet (probably **3** isomerizes to **4**). However, to overcome this problem, products were separated also by silica gel columns (40 cm × 1 cm o.d.) with 4:1 mixture of petroleum ether (60–80) and ether (or acetone), respectively, as eluent. Spectral data for all products are summarized in Table V, except for **8b** and 16–18, which were compared with authentic samples.

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Registry No. **1a**, 556-61-6; **1b**, 542-85-8; **1c**, 628-30-8; **1d**, 592-82-5; **1e**, 1122-82-3; **1f**, 590-42-1; **1g**, 4411-26-1; **2a**, 109-90-0; **2b**, 110-78-1; **2c**, 111-36-4; **2d**, 3173-53-3; **2e**, 1609-86-5; **2f**, 103-71-9; **2g**, 2243-54-1; **3a**, 6320-65-6; **3b**, 108168-82-7; **3b**·$HClO_4$, 108168-89-4; **3c**, 108168-83-8; **3d**, 108168-84-9; **4a**, 103031-01-2; **4b**, 98484-44-7; **4c**, 98492-89-8; **4d**, 108168-85-0; **5a**, 64671-66-5; **5b**, 64671-67-6; **5c**, 64671-68-7; **6a**, 623-95-0; **6b**, 1792-17-2; **7b**, 4411-25-0; **8a**, 1124-53-4; **8b**, 762-84-5; **8c**, 880-52-4; **9a**, 766-93-8; **10**, 32091-48-8; **11**, 110-59-8; **12**, 625-28-5; **13**, 107-92-6; **14**, 108168-86-1; **15**, 108168-87-2; **19**, 108168-88-3; **20**, 630-18-2; **21**, 134-32-7.

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