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THE MECHANISM OF ANODIC OXIDATION OF ALKYL IODIDES. ELECTROPHILICITY OF IODINE(I).

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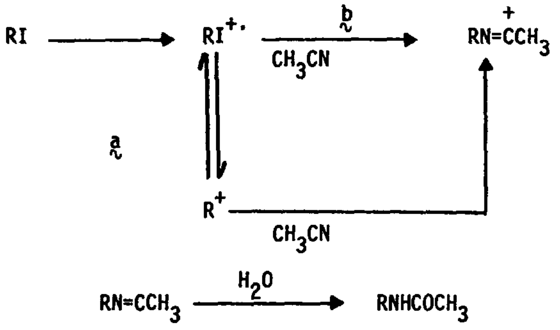
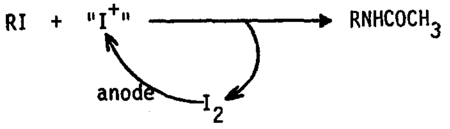
Alkyl iodides form alkyl acetamides when oxidized at platinum in acetonitrile, and the initial study of this process indicated that carbonium ions were intermediates in certain of the reactions.[1] Keating and Skell then studied the oxidation of n-propyl bromide in methanol and suggested that primary alkyl halide oxidations generate hot carbonium ions (path a).[2] Laurent and coworkers[3] have, however, recently gained evidence that an S_N2 type displacement on an initially-formed cation radical is involved in primary alkyl iodide oxidations (path b) in acetonitrile.



The original publication on this subject[1] indicated that plots of i vs t, i vs [RI], and coulometry were not consistent with the simple pathways a or b. The involvement of iodine oxidation was suspected and this was iterated[4] when it was discovered that a stable iodine(I) species could be formed by iodine oxidation under the same conditions employed for alkyl iodide oxidation.[4] We have now demonstrated that an indirect reaction involving iodine(I) and alkyl iodide (path c) contributes significantly to anodic alkyl iodide chemistry.



path c

Iodine(I)[5] was generated by exhaustive (n=2.1) oxidation of I_2 in acetonitrile at 1.8 V and added to acetonitrile solutions of alkyl iodides. Iodine was produced instantaneously and the alkyl acetamide was isolated upon work-up (Table I).

Table I. Reactions Products of Iodine(I) and Alkyl Halides.[a]

Substrate	Product (% Yield)
2-octyl iodide	2-octylacetamide (54) 3-octylacetamide (22)
1-Adamantyl iodide	1-adamantylacetamide (60)
Cyclohexyl iodide	cyclohexylacetamide (45)
n-Propyl iodide	n-propylacetamide (19) isopropylacetamide (12)

a. Addition of 100 ml of a solution 0.2 M in iodine(I) to 25 ml of a solution containing 0.05 moles of alkyl iodide in acetonitrile.

It is known[1,4] and we have confirmed that iodine is oxidized to iodine(I) at the potentials necessary for alkyl iodide oxidation. Since iodine is present in the anolyte the two reactions necessary for c must proceed under the oxidation conditions.

Although essentially all of the alkyl acetamide product could come from path c *via* a high I_2-I(I) concentration near the anode surface the contribution of paths a,b is difficult to determine. It could well change during the course of a preparative oxidation in a divided cell since iodine builds up as alkyl iodide is consumed. We have tried to probe this point by examining the products from S-2-octyl iodide (Table II).

Table II. Product Ratios from Electrolytic and Iodine(I) Reactions.

Substrate	Products	Electrolysis[a]	Iodine(I)[b]
S-2-Octyl iodide	R-2-octylacetamide	53	47
	S-2-octylacetamide	26	24
	3-octylacetamide	21	29
n-Propyl iodide	n-propylacetamide	59	61
	iso-propylacetamide	41	39

a. Electrolysis of 4 mmole alkyl iodide in a divided cell at Pt using 100 ml CH_3CN, $LiClO_4$.

b. Addition of 100 ml of a solution 0.2 M in iodine(I) to 25 ml of a solution containing 0.05 moles of alkyl iodide in acetonitrile.

3-Octylacetamide (∿25%) and 2-octylacetamide (∿75%) are formed in the same yield by both direct oxidation[6] and by reaction with the iodonium species. Furthermore, the stereochemistry of the 2-octylacetamide[7] is essentially identical in both reactions (49% racemization, 51% inversion). This indicates great similarity in the two processes, but does not resolve the problem of how much (if *any* significant amount) of the oxidation involves direct oxidation of alkyl iodide. We have found that this product ratio is not very sensitive to leaving group since acid catalyzed solvolysis of 2-octanol in acetonitrile also gives a similar ratio. In the case of n-propyl iodide an identical isomer ratio was again observed by direct oxidation and iodonium reactions supporting the above conclusions.

Further exploration of the role of water in this process and an explanation of the i,t curves will be reported in a full paper on iodine(I) reactivity.

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REFERENCES

1. L. L. Miller and A. K. Hoffmann, *J. Amer. Chem. Soc*, **89**, 593 (1967).
2. J. T. Keating and P. S. Skell, *J. Org. Chem.*, **34**, 1479 (1969).
3. A Laurent, E. Laurent and R. Tardivel, *Tet. Letts.*, 4861 (1973); A. Laurent and R. Tardivel, *Comp. Rend. Acad. Sci.*, **272**, Series C, 8 (1971).
4. L. L. Miller, E. P. Kujawa and C. B. Campbell, *J. Amer. Chem. Soc.*, **92**, 2821 (1970).
5. The structure of the iodonium species may be $CH_3C\overset{+}{N}I$ or N-iodoacetamide.[4]
6. Oxidation to 1.0 Far/mole and 2.0 Far/mole gave the same isomer ratio and optical purity.
7. The S-2-octyl iodide (α_D^{24} + 41.3°, op. purity 66%) was prepared from R-2-octanol.
8. The 2-octyl acetamide was purified by glc and compared with authentic S-2-octylacetamide (α_D^{20} - 2.516°,op. purity 91%) prepared from the sequence R-2-octanol, R-2-octyl tosylate, S-2-octyl azide, S-2-octylamine, S-2-octylacetamide.