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Zn/OH^- REDUCTIONS OF ORGANIC COMPOUNDS IN DIMETHYLSULFOXIDE ; A NEW SIMPLE METHOD OF PREPARING RADICAL ANIONS

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Summary: A new method of preparing radical anions from a variety of organic substrates is proposed that involves the use of Zn/KOH in DMSO as electron source.

Recently reports from our laboratory[1] and from others[2] have demonstrated the electron transfer character of OH^- in converting readily reducible organic substrates to the corresponding radical anions. We now observe that Zn/OH^- in DMSO is a much stronger reductant than is OH^- alone in that a wide variety of organic molecules with reduction potential upto ca. -2.2 eV are readily reduced to the corresponding radical anions. To test the scope of this reagent, we selected a few substrates from among polynuclear hydrocarbons which yielded deep coloured solutions that gave distinct EPR signals and electronic absorption spectra diagnostic of radical anions having formed (Table 1). A representative reaction is that of perylene(reduction potential = -1.46 eV) (25 mg,0.1 mmol) in DMSO (20ml) with zinc powder(15 mg) and aqueous 6M KOH (5 drops) during 15 min stirring at room temperature. The radical anion formation is marked by the spontaneous appearance of blue colour(λ_{max}578 nm) which attains considerable intensity within the first few minutes of stirring especially when the solution is warmed. On a probe by EPR spectroscopy, a spectrum identical with that reported elsewhere[3] was obtained.

A remarkable feature of this work is the ready formation of radical anions even in the absence of inert conditions. In a test-tube experiment,it was seen that the radical anions once formed disappeared only after vigorous shaking(upon admission of air) and the colour reappeared on warming and allowing the test-tube to stand for some time. It was possible to repeat this exercise a number of times. This is in sharp contrast to alkali metal reductions in ethereal solvents in which case the tolerance of radical anions so formed toward atmospheric oxygen is quite low. Thus reductions using the reagent, Zn/OH^- in DMSO, offer an attractive alternative to the existing methods of preparing radical anions.

Another significance of this reagent is its utility in the reactions of preparative value wherein the initially formed radical anion is short lived and vulnerable to follow-up reactions. Many aspects of such reductions are closely similar to cathodic reductions. For example, aliphatic diazocompounds like 9-diazofluorene and azibenzil are reduced to fluorenone azine and deoxybenzoin respectively in much the same way as in cathodic reductions[4]. Another example of synthetic utility is the reduction of aromatic ketones which takes place within minutes yielding the corresponding alcohols in quantitative yield. In each case, highly coloured solutions are formed whose visible absorption and EPR spectra provide an unequivocal evidence of ketyl radicals being formed. A typical reaction is that of benzophenone(0.91 g,5 mmol) in DMSO (25 ml) with Zn (0.5 g) and aqueous 6M KOH (3 ml) during 20 min stirring at 45°C which upon work-up yields benzhydrol in

97.5 % yield. The solution develops an intense blue colour (λ_{max} 690 nm) diagnostic of benzophenone ketyl (1) being formed which fades out as the reaction progresses. That 1 is indeed the key intermediate and participates in the product forming coordinate was verified by carrying out the reaction in the presence of p-dinitrobenzene (p-DNB), a well known anion radical scavenger. A single electron transfer from 1 to p-DNB occurred and the reaction product was the regenerated ketone and not the alcohol (eq.1).

$$\underset{(1)}{R_2\dot{C}\!-\!\bar{O}} \;+\; \text{p-DNB} \longrightarrow R_2C = O \;+\; \text{p-DN}\overset{\bar{\bullet}}{\text{B}} \;.....\; (1)$$

These results are reminiscent of the mechanism for the elctrochemical reduction[5] of aromatic ketones wherein the follow-up reaction of 1 is considered to involve a further electron addition to 1 followed by protonation to yield the alcohol.

Table 1. Reduction of organic molecules to radical anions with Zn/OH$^-$ in DMSO at 30°C

	Compound	observed λ_{max}(nm) of radical anion	reported λ_{max}	(ref)	Product (yield %)	
1	Perylene	578	578	(6)		
2	Anthracene	660	657	(3)		
3	9,10-Dimethylanthracene	745,696	not found in literature			
4	9,10-Diphenylanthracene	673,612,562	-	(7)		
5	Pyrene	492	495	(8)		
6	Phenazine	512,538,601	516,551,590	(9)		
7	Benzophenone	690	681	(10)	Benzhydrol	(97.5)
8	Fluorenone	545	550	(11)	Fluorenol	(96.3)
9	Xanthone	640	636	(12)	Xanthydrol Xanthene	(58.0) (37.5)
10	Thioxanthone	690	703	(13)	Thioxanthydrol Thioxanthene	(52.5) (41.4)
11	4-Benzoylpyridine	650	663	(14)	Phenylpyridyl methanol	(92.3)

REFERENCES

1. K.L.Handoo, K.Gadru and C.K. Jain , Indian J. Chem., 22B, 526 (1983).
2. (a) T. Abe and Y. Ikegami, Bull. Chem. Soc. Japan, 49, 3227(1976);(b) I.I. Bilkis and S.M. Shein, Tetrahedron, 31, 969(1975); S.M. Shein, L.V. Bryukhovetskaya and T.M.Ivanova, Izv.Akad.Nauk SSSR Ser Khim., 1594, 1601(1973); (c) E.C. Ashby,D.T. Coleman III and M.P. Gamasa, Tetrahedron Lett., 851(1983).
3. E.C. Ashby, A.B. Goel, R.N. DePriest and H.S. Prasad, J. Am. Chem. Soc., 103, 973(1981).
4. (a) D. Bethell, P.J. Galsworthy, K.L. Handoo and V.D. Parker, J.C.S. Chem. Commun., 534(1980);(b) D.Bethell, L.J. McDowall and V.D. Parker, J.C.S. Chem. Commun., 308(1984).
5. P.J. Elving and J.T. Leone, J. Am. Chem. Soc., 80, 1021 (1958).
6. P. Hoijtink and P.W. Weijland, Recl. Trav. Chim. Pays. Bas., 76, 836 (1957).
7. R.E. Sioda, J. Phys. Chem., 72, 2322 (1968).
8. P. Balk, G.J. Hoijtink and J.W.H. Schreurs, Recl. Trav. Chim. Pays. Bas., 76, 813(1957).
9. T. Kato and T. Shida, J. Am. Chem. Soc., 101, 6869 (1979).
10. N. Hirota and S.I. Weissman, J. Am. Chem. Soc., 86, 2538 (1964).
11. V.E. Sahini and L. Ciurea, Rev. Roum. Chim., 14, 1093 (1969).
12. V.E. Sahini, L. Ciurea and Volanschi, Rev. Roum. Chim., 12, 355 (1967).
13. T. Aruga, O.Ito and M. Matsuda, J. Am. Chem. Soc., 101, 7585 (1979).
14. V. Kalyanaraman, C.N.R. Rao and M.V. George, J.Chem. Soc.B.,2406 (1971).

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