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REDUCTION OF QUINONES BY ALLOXANTIN OR ALLOXAN-DERIVED RADICAL

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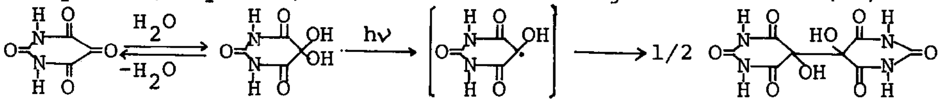
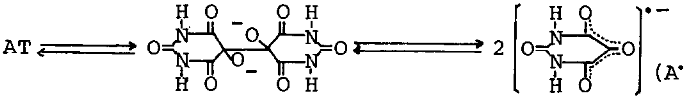
Quinones can be reduced apparently by water mediated by alloxantin (AT) or alloxan radical(A·) produced photochemically from alloxan monohydrate(A-hydrate).

Alloxan(A) is known as one of vicinal tricarbonyl compounds, of which central carbonyl group is so reactive as to form hydrate readily. It has been reported that alloxan monohydrate(A-hydrate) is uv irradiated to give alloxantin(AT) in good yield.[1,2]

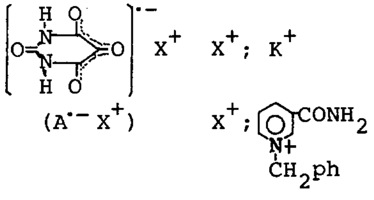


(A) (A-hydrate) (A·) (AT)

Russel etal. have reported that alloxan radical anion($A^{\cdot -}$) is effectively produced by the dissociation of AT in base media.[3]



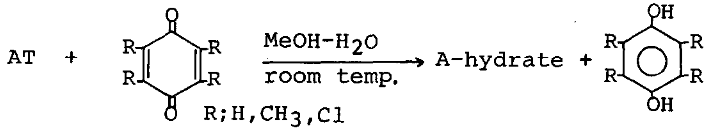
($A^{\cdot -}$)



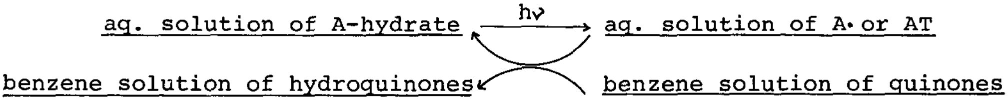
($A^{\cdot -}X^+$)

We have been investigating on the redox behaviour of alloxan in relation to biological electron transfer system, and have reported that alloxan radical anion($A^{\cdot -}X^+$) can be isolated as pyridinium or potassium salts by one-electron reduction of alloxan with 1-benzyl-1,4-dihydronicotinamide (NADH model)[4] or potassium cyanide,[5] respectively.

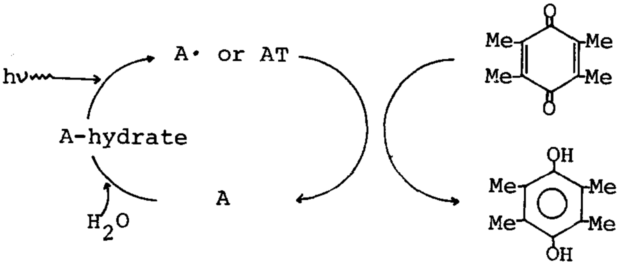
We, in this communication, wish to report the reduction of quinones with alloxan radical(A·), or alloxantin(AT) obtained by photo-irradiation of A-hydrate in aqueous solution, and then the catalytic action of alloxan in the reduction of quinones. It was found that quinones such as p-benzoquinone, tetramethyl-p-benzoquinone(duroquinone) and tetrachloro-p-benzoquinone could be reduced thermally by AT at room temperature in methanol or water to give the corresponding hydroquinones and A-hydrate quantitatively without photo-irradiation(room temp.; 7 hr; quinones= 0.01 M; AT = 0.01 M). Alloxan radical anion salts($A^{\cdot -}X^+$) can also reduce quinones at room temperature without photo-irradiation.[6]



Further, catalytic action of alloxan in the reduction of quinones was examined. Typical procedure is as follows. A solution of 1.64 g(10 mmol) of duroquinone in 100 ml of benzene was added to a solution of 0.16 g(1 mmol) of A-hydrate in 100 ml of water irradiated with a 100W high-pressure immersion mercury lamp for 1 hr in the atmosphere of nitrogen, and the mixture was stirred vigorously at room temperature for 30 minutes. After benzene layer was separated, aqueous solution containing A-hydrate was irradiated again. These operations were repeated 30 times. By this procedure duroquinone was reduced to give durohydroquinone quantitatively. In this experiment, only aqueous solution of A-hydrate was photo-irradiated to avoid the side reactions of quinones by the direct irradiation.



It could be demonstrated from these experiments that alloxan recycled at least 20 times as catalyst in the reduction of quinones, and this finding shows that quinones can be reduced apparently by water mediated by A· or AT produced photochemically from A-hydrate.



References and Notes

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2) Y.Otsuji, S.Wake, and E.Imoto, Tetrahedron, 26, 4139 (1970).
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4) T.Endo and M.Okawara, Chem.Letters, 1977, 1487.
5) T.Endo, A.Kudo, and M.Okawara, Bull.Chem.Soc.Jpn., submitted.
6) T.Endo and M.Okawara, unpublished data. It has been reported that pinacol derivatives can reduce p-benzoquinone or ketones photochemically(A.Shonberg and A.Mustafa, J.C.S. Chem.Comm., 1944, 67. R.S.Davidson, F.A.Younis and R. Wilson, ibid., 1969, 826.).

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