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NUCLEOPHILIC CHARACTER OF ALKYL RADICALS. RATE CONSTANT AND NEW METHODS OF HOMOLYTIC ALKYLATION OF 1,4-BENZOQUINONE

Attilio Citterio

Istituto di Chimica del Politecnico, Piazza L. da Vinci 32, 20133 Milano, ITALY

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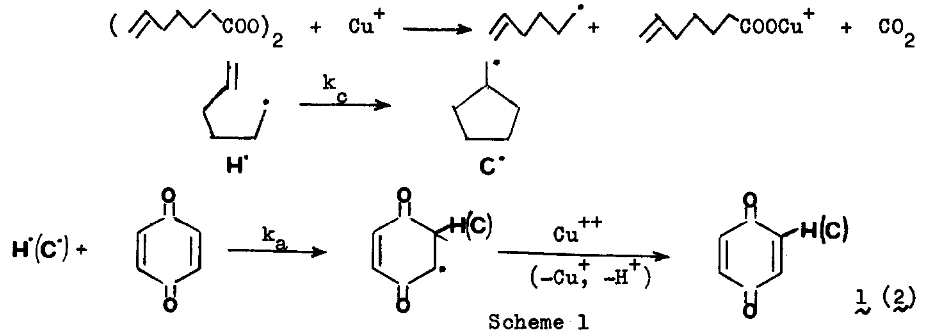
The use of 1,4-benzoquinone as a free-radical scavenger or as an inhibitor of free-radical chain processes is well known, but surprisingly in literature there are no reports of the rate constants for free-radical addition to quinone. The knowledge of these data is especially important with alkyl radicals, because they are intermediates in two of the main free-radical chain processes (autoxidation and vinyl polymerization) in which quinone has proved high inhibition efficiency.

Previous results from this laboratory(1) indicated that primary alkyl radicals are much more reactive toward 1,4-benzoquinone than toward butadiene (for which the rate constant 9.2 10^4 l $mol^{-1}sec^{-1}$ at 25°C was estimated(2)); so, a very high rate constant could be foreseen for quinone addition.

We have determined the rate constant, k_a , by using the kinetic model of Scheme 1, based on the irreversible isomerization of 5-hexenyl radical, $H^{\bullet}$, to cyclopentylmethyl, $C^{\bullet}$,



Scheme 1

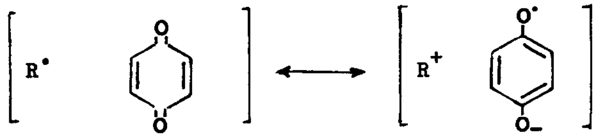
at a rate, k_c , which is known(3), from the relationship(4) (i = initial , f = final) :

$$k_a = k_c \frac{[\mathbf{1}]_f}{[\mathbf{2}]_f} \frac{1}{[\text{Quinone}]_i}$$

At 69°C a mean value of $k_a = (2.0 + 0.7)\cdot 10^7\ M^{-1}sec^{-1}$ was astimated at various quinone concentrations in the presence of $CuOCOCH_3$ (10^{-3} M), $Cu(OCOCH_3)_2$ ($2.5\ 10^{-2}$ M) and di-6-heptenoyl peroxide (10^{-3} M) in CH_3COOH/CH_3CN (3/2) solutions. Preparative g.l.c. (on 5 ft×1/4 in. column packed with OV_{17} 10% on chromosorb W (60-80 mesh) at 160°C of the reaction mixture gave the products **1** {m.p. 35-37°C; MS m/e : 190, 123; $\delta^{CDCl_3}_{TMS}$ 6.72 ($s,H_{6,5},2H$), 6.58 ($s,H_3,1H$), 5.8-4.8 ($m,CHCH_2,3H$), 2.4 ($t,CH_2Ar,2H$), 1.5-2.2 (m,6H)} and **2** { m.p. 40-41°C ; MS m/e : 190, 123; $\delta^{CDCl_3}_{TMS}$ 6.7 ($s,H_{6,5},2H$), 6.6 ($s,H_3,1H$), 2.5 ($d,CH_2CH,2H$), 1.1-2.1(m,9H)}.

By comparison with the rate constant data(5) for the addition of the same radical to the main "spin traps" (phenyl-N-t-butyl-nitrone, $k_a = 1.3\ 10^5\ M^{-1}sec^{-1}$ and 2-methyl-2-nitrosopropane, $k_a = 9\ 10^6\ M^{-1}sec^{-1}$ at 40°C) 1,4-benzoquinone appears to be an effective scavenger of primary alkyl radicals.

A similar high rate constant is not observed with electrophilic radicals : in fact, amino-radical-cations do not react with 1,4-benzoquinone(6) and oxygen-centered radicals react faster in hydrogen abstraction or with olefins(7) and homocyclic aromatic (as shown by the syntheses below) than with 1,4-benzoquinone. Moreover, electron-withdrawing substituents on quinone ring favour methyl radical addition(8). This suggests that an extensive degree of charge-transfer in the transition state (structure III), owing to the nucleophilic character of alkyl radicals, contributes in decreasing the activation energy of the process.

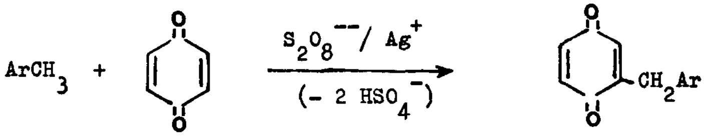

(III)

A further indication concerns the synergism of the inhibition of the quinone-hydroquinone system in free-radical chain reactions such as autoxidation, in which alkyl and alkyl-peroxy radicals are involved : quinone reacts faster with the first ones and hydroquinone with the second ones leading to similar intermediates.

The high rate constant of the alkyl radical addition to 1,4-benzoquinone allows to overcome other possible side reactions and to achieve the following new types of clean homolytic alkylation

i) Homolytic benzylation.

Benzyl radicals can be obtained efficiently by electron-transfer oxidation of alkylbenzenes by peroxydisulfate(9). Their easy oxidation often prevents from the attack to other substrates; however, in the presence of quinone, the addition reaction successfully com petes with the oxidation and high yield of 2-benzyl-1,4-benzoquinone is obtained (eq. 1).

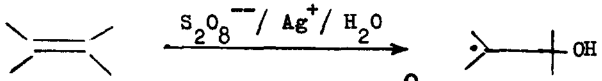


(1)

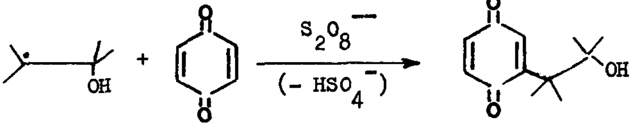
In a typical experiment, a solution of $Na_2S_2O_8$ (0.1 mole) in water (60 ml) was added in 2 hrs under stirring to a two phase system of 1,4-benzoquinone (5.4 g, 0.05 mole) in toluene (60 ml) and $AgNO_3$ (0.7 g) in water (70 ml), warmed at 70°C. Separation of toluene layer and extraction with ethyl ether gave, after concentration, a residue from which 2-benzyl-1,4-benzoquinone (8.7 g, 88% yield) was purified by chromatography on SiO_2 and crystallization from methanol-water (m.p. 42°C). Only small amounts of dibenzyl derivative occur under these conditions (1%).

ii) <u>β-hydroxyalkylation</u>.

Olefine oxidation by the system silver ions/ peroxydisulfate gave β-hydroxyalkyl radicals(10) which are trapped by quinone according to the equations 2 and 3.



(2)



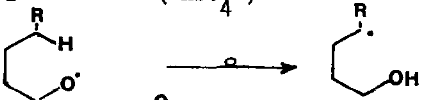
(3)

Under conditions similar to those previously described for toluene, cyclohexene gave a mixture of cis- and trans-2-(2-hydroxy-cyclohexyl)-1,4-benzoquinone (40 : 60) in 70% yield) and 2-(2-cyclohexenyl)-1,4-benzoquinone (10%). Similar results (40-70% yield) were obtained with other internal olefins. No styrene polymerization was observed under these conditions and 2-(2-hydroxy-1-phenylethyl)1,4-benzoquinone was isolated by chromatography (11) (15%).

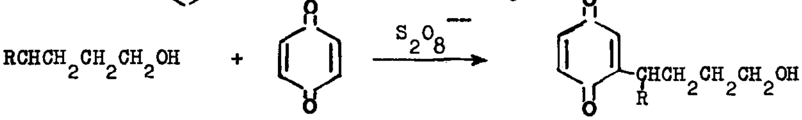
iii) <u>δ-hydroxyalkylation</u>.

Oxidation of long chain alcohols by the system $S_2O_8^{--}/\ Ag^+$ (12) in the presence of quinone gave δ-hydroxyalkyl-1,4-benzoquinone according to the equations 4, 5 and 6.

$$RCH_2CH_2CH_2CH_2OH \xrightarrow[(-HSO_4^-)]{S_2O_8^{--}/\ Ag^+} RCH_2CH_2CH_2CH_2O^\bullet \qquad (4)$$



(5)



(6)

An example is offered by the oxidation of 1-hexanol. A solution of $Na_2S_2O_8$ (0.01 mole) in water (10 ml) was added under stirring to a heterogeneous mixture of $AgNO_3$ (0.2 g) in water (40 ml) and quinone (10^{-2} mole) and 1-hexanol (0.04 mole) in hexane (5 ml) at 60°C. Extraction with ethyl ether, evaporation and distillation under reduced pressure gave a residue which was chromatographed on SiO_2 with hexane/ether (9:1) to give 0.62 g (33%) of 2-(1-ethyl-4-hydroxybutyl)-1,4-benzoquinone $\{$ m.p. 31°C ; MS m/e : 208, 190, 161; $\delta_{TMS}^{CDCl_3}$ 6.55 (s,H_3,1H), 6.70 (s, $H_{4,5}$,2H), 3.6 (t,CH_2CH, 2H), 2.8 (m,CH ,1H), 2.3 (broad,OH,1H), 0.9-1.7 (m,9H) $\}$.

Several other sources of nucleophilic carbon-centered free-radicals are in progress in order to extend further the synthetic applications of the homolytic substitution in quinone series.

I thank Professor F. Minisci for discussion.

FOOTNOTES AND REFERENCES

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4) The kinetic derivation of this relationship will be reported elsewhere; for the copper (1) catalyzed decomposition of di-6-heptenoyl-peroxide see A.Citterio, F.Minisci, O. Porta and G.Sesana, J. Amer. Chem. Soc., 99, 7960 (1977).

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