MECHANISM OF THE γ-RADIOLYSIS OF 2-PROPANOL SOLUTIONS OF CYCLOHEXANONES

E. ALIPOUR, D. VIDRIL, J. C. MICHEAU and N. PAILLOUS and A. LATTES Laboratoire des Intéractions Moléculaires et Réactivité Chimique et Photochimique, E.R.A. au CNRS No. 264, Université Paul Sabatier, 31062 Toulouse Cedex, France

L. GILLES

Commissariat à l'Energie Atomique, Département des Programmes, 33, rue de la Fédération, 75 751 Paris Cedex 15, France

and

J. MATHIEU

Laboratoire de Chimie Analytique Appliquée, Ecole Nationale Superieure de Chimie, INP, 118,, route de Narbonne 31077 Toulouse Cedex, France

(Received in France 6 July 1982)

Abstract—The γ -radiolysis of 2-propanol solutions of cyclohexanone gives mainly hydrogen, acetone, pinacol, methane derived from 2-propanol, and cyclohexanone, 2-(2-cyclohexanonyl)-cyclohexanone, and 3-(2-hydroxy-2-propyl)cyclohexanone derived from cyclohexanone. The radiolytic yields of all these products were highly dependent on the initial cyclohexanone concentration. The formation of cyclic alcohols by radioreduction has been extended to various substituted cyclohexanones. Radiolytically generated solvated electrons are scavenged by cyclohexanone, leading to the corresponding radical anions. The protonation of these radical anions gives rise to cyclohexanol via the dismutation of the hydroxy-cyclohexyl radicals. Steady state radiolysis measurements were complemented by pulse radiolysis in dilute solution. It was established that radical-anions and hydroxylated radicals decayed according to a second order rate law. When ketone concentration was lower than 0.1M, radiolytic yields were in agreement with the mechanism mentioned above. However, in concentrated media the large increase in G(cyclohexanol) cannot be only accounted for by the involvement of radiolytically generated solvated electrons; probably it is due to an electron transfer from the cyclohexanone enolate to cyclohexanone itself, thus generating extra amounts of cyclohexanone radical anions.

In a general investigation of the reactions of cyclic ketones, induced by radiations, the γ -radiolysis of 2-propanol solutions of cyclohexanones was undertaken.^{1a} As the behaviour of the same mixtures irradiated by UV light has been studied previously,^{1b} it was of interest to attempt to initiate the same reactions by ionizing radiations. Carbonyl compounds are usually used in γ -radiolysis experiments as electron scavengers, however the structures and the radiolytic yields of the final products resulting from this capture have not been very precisely characterized. The most extensive investigations on these reactions were carried out only in the particular case of the radiopinacolisation of benzophenone in alcoholic solution.²

RESULTS

The γ -radiolysis of pure 2-propanol leads to the formation of products such as hydrogen, methane, acetone, acetaldehyde and 2,3-dimethyl-2,3-butanediol (pinacol).³

Addition of cyclohexanone modifies the radiolytic yields of all these compounds and simultaneously gives rise to the formation of cyclohexanone oxidoreduction by-products such as cyclohexanol, (2cyclohexanonyl)cyclohexanone, and 3-(2-hydroxy-2-propyl)cyclohexanone. We have systematically investigated the radiolytic yields of all the main products which are formed during the γ -radiolysis of cyclohexanones 2-propanol mixtures. The concentration of these mixtures were varied from pure-2 propanol to neat cyclohexanone.

Figure 1 shows that radiolytic yields depend strongly on the cyclohexanone concentration.

This radioinduced reaction has been extended to many substituted cyclohexanones. As in the case of cyclohexanone the radioreduction yield-G-(cyclohexanol) increases with the concentration of the corresponding cyclic ketones. A second series of results from other cyclanones is shown in Fig. 2.

DISCUSSION

This radioreduction reaction which until now has only been reported for benzophenone, appears to be general. The reaction mechanism can now be considered.

Mechanism in dilute medium. A survey of the recent literature⁴ suggests that the first step of the radioreduction reaction is the ketone radical-anion formation by electron scavenging (reaction 1)

Competitive experiments using well known electron scavengers⁵ support this assumption; as shown in





Fig. 1. Radiolytic yields of main products issued from the radiolysis of cyclohexanone 1/2-propanol mixtures vs initial ketone concentration.



Fig. 2. Radiolytic yields of various cyclohexanols vs initial cyclic ketone concentration.

[naphthalene] M	10 ⁻³	5x10 ⁻³	10-2	5×10-2
G(cyclohexanol) [cyclohexanone] = 10 ⁻² M	0.80	0.80	0.72	0.39
[Li NO3] M	7x10-3	2.4×10 ⁻²	7.1×10-2	16x10-2
G(cyclohexanol) [cyclohexanone] = 0.2 N	2.20	2.10	1.95	1.60
[сн ₃ ю ₂] м	3.2x10-3	1.9×10 ⁻²	7.4×10-2	19x10-2
G(cyclohexanol) [cyclohexanone] = 0.2 M	2.25	2.15	1.95	1.10



Table 1, lithium nitrate, nitromethane or naphthalene quench the formation of cyclohexanol.

In the following step, the protonation of the cyclohexanone radical-anion leads to the hydroxycyclohexyl radical (reaction 2). The presence of such species was confirmed by radical trapping with 1-hexane (reaction 3).

As it was previously established for the photoreduction process,⁶ the disproportionation of the hydroxycyclohexyl radicals gives cyclohexanol (reaction 4). Cyclohexanol can also be formed by the disproportionation of radical-anions (reaction 5) followed by the protonation of the alcoholate (reaction 6). This disproportionation reaction 5 has been previously demonstrated by Rautenstrauch and Geoffroy⁷ for chemically generated cyclohexanone radical-anions.

To provide further confirmation of these mechanisms all the postulated species were monitored by pulse radiolysis, and characterized by their absorption spectra.

Solvated electrons are known to display a very broad absorption band with a maximum at 820 nm in 2-propanol.⁸ Decay curves were recorded for various ketone concentrations. The observed pseudo first order rate constant for electron capture by cyclohexanone in 2-propanol ($k_c = 4.5 \pm 0.6 \times 10^9 \,\mathrm{M^{-1}}$ s⁻¹), is slightly lower than the values found either by Toffel *et al.*⁹ or by Anbar *et al.*¹⁰ for cyclohexanone in aqueous solution ($k_c =$ $7.8 \times 10^9 \,\mathrm{M^{-1} \, s^{-1}}$). However, it is very close to the value found for acetone in ethanol¹¹ ($k_c =$ $4.7 \times 10^9 \,\mathrm{M^{-1} \, s^{-1}}$). All these values are of the same order of magnitude as the diffusion rate constant in alcoholic media.

$$k_{\rm diff} \simeq 4.6 \times 10^9 \,{\rm M}^{-1}{\rm s}^{-1}$$

Radicals were observed by monitoring pulse radiolysis experiments at lower wavelengths. In N₂O saturated 2-propanol the major absorbing species between 250 and 300 nm is the hydroxyisopropyl radical. This radical decay is by second-order kinetics (reaction 7). The corresponding deactivation rate constant $(2 \text{ k}_m/\epsilon)$ has been calculated for various wavelengths. Assuming the value given by Simic and Hayon for 2 k_m to be $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ the hydroxy isopropyl radical spectrum can be estimated (Table 2).

As has been pointed out by Toffel et al.⁹ the decay of the cyclohexanone radical-anion or of the corre-



Table 2. Molecular absorption coefficients of hydroxyisopropyl radicals

እ nm	250	275	300	325	350
E (x 10 ⁻³)	5.6	2.6	1.6	. 5	. 1

sponding hydroxylated radical can also be observed by pulse radiolysis. The major species absorbing at 450 nm is the radical-anion of cyclohexanone. In fact, the hydroxylated radicals do not absorb significantly at this wavelength. The kinetic behaviour of these radical-anion obeys a second order rate law $(2 k_m/\epsilon = 1.7 \times 10^7 \text{ cm.s}^{-1})$ consistent with either a charge neutralization (reaction 2) or a disproportionation (reaction 5).

All these experimental data support a mechanism of electron scavenging by cyclohexanone followed by disproportionation of radical species (hydroxylated radicals or radical-anions). The data are in good agreement with a quantitative analysis of the radiolytic yield G(cyclohexanol) providing that the cyclohexanone concentration is lower than 0.1 M. In fact, the scavenging of one solvated electron leads to the formation of one hydroxycyclohexyl radical which gives only half a cyclohexanol molecule by disproportionation. Now the various G_{er} found in the literature¹³ are generally sightly lower than 4, so that the corresponding G(cyclohexanol) could never be greater than 2 under these conditions. If, in dilute medium the G(cyclohexanol) is less than 2, this will no longer be the case when the cyclohexanone concentration increase.

An other competitive reaction mechanism also leading to cyclohexanol formation and whose efficiency increases as the ketone concentration becomes greater is probably involved.

Mechanism in concentrated medium. Three main hypotheses concerning this new process can be suggested. They necessarily involve either (a) an excited state of cyclohexanone; (b) a radical propagation reaction; or (c) a monoelectronic transfer reaction. The kinetics of all these reactions are in qualitative agreement with a ketone concentration dependence.

Excited states of cyclohexanone could arise either by energy transfer from excited solvant (G(solvent excited states) remaining however very low¹⁴) or by geminate neutralization of the corresponding radicalions. A comparison between results obtained either by photolysis or γ -radiolysis of 2-substituted ketones allows us to rule out this hypothesis. If UV irradiation of not 2-substituted cyclohexanones induces cyclohexanol formation,¹⁵ it is no longer the case for 2-substituted cyclic ketones which undergo Norrish type I cleavage from the triplet state.¹⁶

As no cleavage products (ethylenic aldehyde or ester) were detected in the γ -radiolyzed 2-methyl cyclohexanone/2-propanol mixtures there is no evidence that a triplet state (if generated) is responsible for cyclohexanol formation.

Several radicals are generated during the γ -radiolysis of 2-propanol (H', CH', CH', CH', COHCH,, etc.) All these species are able *a priori* to react with cyclohexanones. As has been suggested elsewhere for acetone^{3b} where the ratio k_{abd}/k_{add} is about 4 ± 1 the reaction between H' and a ketone is more likely a hydrogen abstraction than an addition. As $G(CH_4)$ does not depend on the ketone concentration, the methyl radicals which are the parent species of methane are probably not involved in the radioreduction process.

In order to investigate the role of oxygenated radicals in the radioreduction process, we have checked their reactivity towards cyclohexanones.

Hydroxyisopropyl or isopropoxy radicals were generated¹⁷ in the presence of cyclohexanone at room temperature. In neither case, could cyclohexanols nor the corresponding hydroxycyclohexyl radicals be detected, thus demonstrating the inefficiency of this reaction.

As mentioned above chemically generated cyclohexanone radical-anions undergo disproportionation, leading to the formation of the corresponding enolate and alcoholate anions⁷ (reaction 5).

This enolate anion may act as an electron donor towards cyclohexanone. Such a monoelectronic transfer between an enolate-anion and a suitable acceptor has been shown to occur in the case of





oxygen.¹⁸ This result is in good agreement with the low electron affinity of enolate-anion found by Zimmerman *et al.*¹⁹ This monoelectronic transfer reaction could be considered as the trigger step of the radioreduction mechanism in concentrated medium (reaction 10).

This reaction leads to the formation of radicalanions as does the direct scavenging of radiolytic solvated electron. The overall stoichiometry of both reactions requires that one radical-anion is enough to provide one alcoholate, and consequently one cyclohexanol. Whereas, the classical mechanism in dilute medium requires two radicals anions for the formation of one cyclohexanol. Therefore, the involvement of the above mentioned mechanism can explain the high value of G(cyclohexanol) at high ketone concentrations.

Various other experimental results support this assumption. The presence of the diketone can be explained by the dimerization of α -cyclohexanonyl radical resulting from the reaction 10:



Moreover, all the factors promoting the enolateanion formation will increase at the same time the G(cyclohexanol) but only for enolizable ketones. We have therefore investigated the influence of alkaline medium either on enolizable cyclic ketones (cyclohexanone), or non-enolizable ones (fenchone).

Table 3 shows that both cyclohexanol and (2-

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cyclohexanonyl)cyclohexanone increase with $[OH^-]$ in case of cyclohexanone but not in the case of fenchone. These results agree with the involvement of enolate anions in the radioreduction process. For fenchone no coupling products could be detected and the decrease of G(fenchol) may be due to the slowingdown of protonation with higher pH values. This effect which also occur in the former case suggests that the monoelectronic transfer reaction could be more efficient than previously expected.

This transfer, which is probably thermostimulated can be tested independently from the radiolytic process. When enolate-anions are chemically generated in highly alkaline (KOH \sim 5M) cyclohexanones and 2-propanol mixtures, low but significant amounts of cyclohexanols are detected. It is the case for cyclohexanone, 3,3,5-trimethylcyclohexanone, 2-methyl cyclohexanone and t-butyl-4 cyclohexanone, but not for fenchone as expected.

In summary, the mechanism of the radioreduction consists essentially of following steps: elementary reactions of the radiolysis of pure 2-propanol; interaction of the reactive species thus generated, with cyclohexanone; monoelectronic transfer between enolate-anions and cyclohexanone. This mechanistic scheme can explain the changes in the radiolytic yields of the various final products which have been observed: the decrease of $G(H_2)$ results from the scavenging of solvated electrons (parent species of hydrogen) by cyclohexanone; the fact that $G(CH_4)$ does not vary, due to the lack of reactivity of CH_j towards cyclohexanone; pinacol formation results from the symmetric coupling of hydroxyisopropyl radicals. When this reaction competes with interactions between cyclic and aliphatic radicals, G(pinacol) decreases while G(acetone) increases. The

Table 3. Effect of OH⁻ on the y-radiolysis of ketone/2-propanol mixture

-Enolizable	ketone:	cyclohexanone	[.3M]	
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[KOH]	0	10 ⁻⁴	10-3	5.10-3
G(cyclohexanol)	$2.5 \pm .1$	$2.4 \pm .1$	2.55 ± .1	$3.8 \pm .1$
G(diketone)	1.05 ± .1	$1.5 \pm .1$	$2.0 \pm .1$	$2.1 \pm .1$

b)-Non-enolizable ketone: fenchone 7 [.1 M]

[кон]	0	10-4	10-3	10-2
6 (fenchols)	1.07 ± .05	.90 ± .03	.33 ± .02	.08 ± .05

increase of G(cyclohexanol) is initially due to an increasingly more efficient electron capture by cyclohexanone, and then to a greater contribution of the monoelectronic transfer mechanism. The increase of G(diketone) results from the monoelectronic transfer followed by coupling of cyclohexanonyl radicals. In a same way the ketol can also be considered as a by-product of the monoelectronic transfer if we assume a tautomeric equilibrium between α and β cyclohexanonyl species followed by coupling with hydroxyisopropyl radicals. In highly concentrated medium all the G-values are strikingly modified by direct y-radiolysis of cyclohexanone.

CONCLUSION

A new radioreduction reaction was investigated in the cyclanic series. This reaction which has been extended to many cyclohexanones appears to be general. In spite of the complexity of the radiolytic mixtures we have outlined the most efficient radioreduction steps both in dilute and concentrated media. In particular, we have established the involvement of a new reaction mechanism that has been overlooked. The dependence on G(cyclohexanol) on concentration and pH, supports the participation of a monoelectronic transfer between the cyclohexanone enolate-anion and the cyclohexanone itself.

EXPERIMENTAL

The ⁶⁰Co γ -source was a gammacell 220, the dose rate being approximatively 382 Gy h⁻¹. Doses were determined by classical Fricke dosimetry.²⁰ Irradiation time was between 35 and 800 h. *G*-values were corrected taking into account the average electronic density of the mixture and extrapolated to 0% in reaction progress.

Starting materials

Irradiation

Cyclohexanone, 2-methylcyclohexanone, fenchone and camphor (Fluka purissimum grade) were used without further purification. 3,3,5-Trimethylcyclohexanone, 1hexane, and norboranone were doubly distilled on a Büchi spinning band column. Naphthalene was recrystallized several times from ethanol, and 4tert-butylcyclohexanone from ethanol: water (50:50). 2-Propanol used for hydrogen measurements (Merck spectroscopic grade) was submitted to a further purification; it was refluxed for 36 h with acidified 2,4-dinitrophenylhydrazine, then distilled. Both operations were carried out under argon.

Sample preparation

3 cm³ of solution were placed in a Pyrex tube (16 mm in diameter) degassed at 10^{-*} torr by the freeze/pump/thaw method, then vacuum sealed and irradiated at room temperature. All the radiolytic products were analyzed by gas chromatography. A previously described special device was used for H₂ measurement.²¹ Column A: molecular sieve 5 Å, 4.5 meters long, $T = 50^{\circ}$, vector gas N₂, catharometer detector. For CH₄ measurements: Column B: UCCW 982, 2 metres, room temperature, vector gas He, flame ionisation detector. Liquid products: Acetone yield was determined on a Hewlett-Packard 5750 G chromatograph. Column C: Ucon polar 6%, KOH 3% on chromosorb W 80/100; 4.5 m, temperature 30°, internal standard: heptane. All other liquid products were measured on an Intersmat 120 IFL gas chromatograph equiped with a LTT ICAP 5 integrator. Column C or column D: DEGS 20% on chromosorb W 60/80, 3 m long, temperature 60-180° internal standard: naphthalene or butyrophenone.

Radiolysis of ketone/2-propanol mixtures in presence of an additive

(a) Scavenging of free radicals by 1-hexene. Solutions (1M) of cyclohexanone in the 2-propanol/1-hexene mixture (from 90/10 to 50/50 v/v) were treated according to the previously described schedule. Coupling products were identified by coinjection with authentic samples on both columns C and D.

(b) Base addition. Appropriate quantities of a 2% KOH in 2-propanol were added to cyclohexanone and 2-propanol mixtures using a microsyringe in order to obtain the desired final base concentration. For each run, four identical samples were prepared, two of which were irradiated and the others were used as blanks.

Synthesis of reference products

(a) Synthesis of cyclohexanols. All the cyclohexanols were synthesized from the parent cyclohexanone by classical LiAlH₄ reduction in anhydrous ether.²²

(b) Tertiary alcohol preparation. 1-Hexylcyclohexanol, 1-hexyl 2-methylcyclohexanol and 2-methyl 2-octanol. 8.2 g of 1-bromohexane in 100 ml of anhydrous ether was added dropwise to a suspension of 1.2 g magnesium in 100 ml anhydrous ether. Then after starting the Grignard reaction, 0.05 mole of ketone in 50 ml anhydrous ether was added. The mixture was refluxed for 10 h, then cooled and hydrolyzed by saturated NH₄Cl solution. Etheral extracts were dried over Na2SO4. Residual products were purified by preparative gas chromatography using a Carlo Erba apparatus. Column P: Ucon polar 10%, KOH 10% on Chromosorb W 60/80, temperature 120-180° vector gas N2. 1-Hexylcyclohexanol: Mass spectrum, m/e 184 (M⁺) 166, 141, 127, 99, 81. ¹H NMR (CCl₄): δ ppm/TMS: 3.22 (OH); 1.20 (CH₂); 0.96 (CH₃). 1-Hexyl-2-methylcyclohexanol, Mass spectrum, m/e 197 (M-1), 180, 155, 141, 128, 113. ¹H HMR (CCl₄): δ ppm/TMS: 1.40 (m.unresolved), .84 (CH₃). 2-Methyl-2-octanol: Mass spectrum: m/e 144 (M⁺), 129, 111, 85, 83. ¹H NMR (CCl₄): δ ppm/TMS: 3.18 (OH); 1.16 (gem dimethyl); .90 (CH₃).

(c) Photochemical synthesis of 2-cyclohexanonyl 2cyclohexanone. A mixture of cyclohexanone and t-butyl peroxide (50/50 v/v) was irradiated at 300 nm after nitrogen bubbling in a Srinivasan Rayonet B photochemical reactor. After irradiating 100 h the yellow solution was analyzed by preparative gas chromatography on a Carlo Erba apparatus column P, T = 180°. Mass spectrum: 195 (M⁺), 176, 148, 137, 98. ¹³C NMR (CDCl₃): δ ppm/TMS: 25.2, 26.72, 29.16, 41.69, 50.29, 208.5; 25.58, 28.04, 30.13, 42.26, 49.03, 209.6. Each of the six lines was split showing the presence of two diastereoisomers in non-equivalent proportion.

Structure determinations

3-(2-hydroxy-2-propyl)-cyclohexanone was identified by mass, ¹H and ¹³C NMR spectroscopy. Mass spectrum: m/e156, 141, 98, 97, 83, 70, 69, 67, 59. ¹H NMR (C_6D_6): δ ppm/TMS: 1.20 (gem dimethyl); 3.25 (OH); 2.15 (cycle, unresolved). ¹³C NMR (C_6D_6): δ ppm/TMS: 22.5, 26.2 (CH₃), 26.8 (C_3), 27.4 (C_4), 41.2 (C_6), 43.4 (C_2), 49.9 (C_3), 71.3 (COH), 210 (CO). Assignments were performed by comparison with spectra of authentic samples of various substituted t-butyl cyclohexanones. IR (KBr) (cm⁻¹): 3440, 1740.

Pulse radiolysis

The irradiation source was a Febetron FEB 707 (1.75 MeV; 8 ns). The absorbed dose was around 100 krads/cm²/pulse. The optical system included a grating monochromator and a 450 W XBO Xenon lamp. The intensity of the latter could be increased during the analysis. The photomultiplier was a Hamamatsu R 446. The irradiation cell was constructed of 1 mm thick suprasil. The optical pathlength was 2.5 cm.

Cyclohexanol formation in highly alkaline medium

5M KOH/2-propanol solutions were obtained by stirring

KOH pellets in pure 2-propanol. The yellowish alkaline solution was then carefully mixed with the cyclohexanones in order to provide a ketone concentration about 2M. The homogeneous reaction medium was kept in the dark at room temperature for 4 hrs, then chromatographed (column A; t°: 120°). Cyclohexanone, 3,3,5-trimethylcyclohexanone, 2-methylcyclohexanone, t-butyl 4-cyclohexanone gave rise to the corresponding diastereoisomeric cyclohexanols with a 3 to 8% yield. They were identified by conjection using authentic samples. The same experimental procedures when applied to fenchone did not lead to the expected fenchols.

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