

3.6 Selecting Ethanol as an Ideal Organic Solvent Probe in Radiation Chemistry γ -radiolysis of Acetone-ethanol System and Acetophenone-ethanol System

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ABSTRACT: Radiolysis of acetone-ethanol solution and acetophenone-ethanol solution has been studied in this work. The dependences of G values of the final γ radiolysis products such as H_2 , 2,3-butanediol and acetaldehyde on additive concentration in liquid ethanol have been obtained. There are two kinds of new final products, isopropanol and 2-methyl-2,3-butanediol are detected in irradiated acetone-ethanol solution. As for acetophenone-ethanol system, more new final products are found.

In addition, experiments of pulse radiolysis upon acetophenone-ethanol solution have also been performed. The absorption spectrum with λ_{max} at 315nm and 440nm is observed, which is assigned to ketyl radical ion $C_6H_5(CH_3)CO^-$. And the reaction mechanism of the two systems is proposed respectively with a moderate success.

Keywords: Radiolysis, Probe, Acetone, Acetophenone, Disproportionation

INTRODUCTION

Developing the theory of radiation chemistry requires accurate knowledge of the yields of intermediates and final products in irradiated systems. Radiation chemistry of water has been studied extensively and abundant experimental data have been obtained over a great variety of conditions^[1,2,3]. The wealth of theoretical and experimental information makes water a useful model to predict the reaction mechanism of H , e^-_{aq} and OH with organic compounds. Now, many biological compounds are hydrophobic and they are not soluble in water. Therefore, the radiolysis of cyclohexane^[4,5,6], which is a symmetrical nonpolar organic media, has been extensively investigated due in part to the fact that all C-C bond and all C-H bond are equivalent in cyclohexane, it means fewer numbers of products are obtained comparing with that of the straight-chain hydrocarbon. Meanwhile, the majority of biological compounds are still insoluble in cyclohexane, therefore, the application of cyclohexane as a model in radiation chemistry is confined. Since the 1960's, radiation chemists have shown great interest in the radiolysis of ethanol and a lot of experiments have been carried out^[7,8,9,10]. Being a classical polar organic solvent, ethanol shares some similarity with water in radiation chemistry. For example, both of their polar character has influence on the solvation and reactions of the electron and other charged species produced upon irradiation. The predominant advantage of liquid ethanol is that most of the organic compounds are easily soluble in ethanol. Nevertheless, many previous experiments performed often employed various additives as probe to study the behaviour of transient species such as e^-_{solv} , H and α -hydroxyethyl, little has been done to survey the products resulting from the reaction of additive with intermediates. Therefore, it is often difficult to achieve a material balance between final products and intermediates, which may lead to an incorrect interpretation of the established mechanism. Recently, by using styrene, MPP and acrylic acid as additives^[9,11,12], Wu found that α -hydroxyethyl radical did not undergo disproportionation in liquid ethanol and the reaction mechanism was proposed. Later, using acetone as additive^[13], Zhang has studied the dependences of the major final products on acetone concentration and started on surveying the products resulting from the reaction of acetone and intermediates of irradiated ethanol. A new final product, 2-methyl-2,3-butanediol is obtained. However, the material balance is still unresolved and the obtained ratio of rate constants $k(e^-_{solv} + CH_3CHO/e^-_{solv} + CH_3COCH_3) = 5$ is inconsistent with that of obtained from pulse radiolysis experiments, and it seems abnormal for ketone to capture solvated electron in ethanol solution comparing that in aqueous solution. The purpose of this paper is in hope of clarifying the reaction mechanism by re-examining the study of acetone-ethanol system and identifying that ethanol can act as an ideal organic solvent in radiation chemistry. It can be further used as solvent probe in acetophenone-ethanol solution. Because of the structure similarity between acetophenone and flavonoids, our purpose of this work is to present the results and to gather all the information in order to use the radiolysis of the acetophenone-ethanol system as a tool for studying the flavonoid radical chemistry and the

pharmacological function of flavonoids.

EXPERIMENTAL

Absolute ethanol and acetone(Beijing Chemical Plant) were used after purification. The aldehyde content was reduced less about 10^{-6} mol dm^{-3} . The samples were deaerated with high purified nitrogen gas(>99.99%), irradiated at about 20°C with ^{60}Co γ -ray at dose rate 2.0Gy s^{-1} . The yield of hydrogen was determined by GC (instrument: Shimadzu GC-9A; column: 5A molecular sieve; detector: TCD; carrier gas: nitrogen). Those of 2,3-butanediol and acetaldehyde were also performed with GC(instrument: Shimadzu GC-9A; column: PEG, 2m glass column; detector: FID; a special column: chromosob106 for detecting C_2 - C_3 alcohol was employed.)

Acetophenone(A.R.) was used as supplied after purification. The new radiolytic products were detected also with Shimadzu GC-9A(column: OV-1, 2m glass column). Shimadzu GC-14A MS (column, OV-1 25m capillary column, FID detector) was used to identify the P1, P2 P3 and P4.

The pulse radiolysis was carried out using a Van de Graff 2.8 Mev electron generator(High Voltage Eng. Co.) delivering 0.4 μs electron pulse of 1-50Gy in the Max-Planck Institute of Germany. The pulse radiolysis set-up and detection techniques have been described in detailing^[19]. Dosimetry was performed by the SCN⁻ method(0.01 mol dm^{-3} KSCN, N_2O -saturated) using $G((\text{SCN})_2^-)=6.0$ and $\epsilon_{480}=7600$ mol⁻¹ dm^3 cm^{-1} . Unless otherwise stated, dose per pulse used was around 1Gy.

RESULTS AND DISCUSSION

I. THE γ -RADIOLYSIS OF ACETONE-ETHANOL SYSTEM

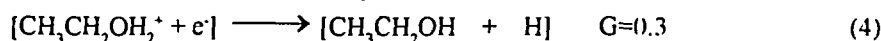
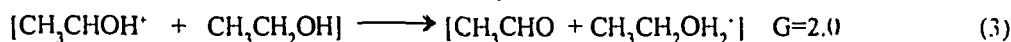
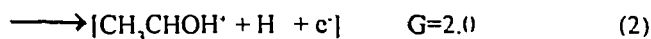
The yields of the three major products, hydrogen, acetaldehyde and 2,3-butanediol are plotted as functions of the concentrations of acetone C in Fig. 1. The most remarkable result is that acetone inhibits the formation of 2,3-butanediol and unaffected hydrogen, while the $G(\text{CH}_3\text{CHO})$ values rise significantly with increasing acetone concentration. All of these are approximately consistent with the results obtained by Zhang.

In addition, two new final products are found. One of the products has been detected by using gas chromatography and GC-MS[M/Z 59(100), 45(10), 71(10), 89(8)]. As for isopropanol, it is identified with the standard compound which appears in the same region. And depending on the known concentrations of the two standard compounds, the G values of the two products are calculated, both of them increases with the increasing concentration of acetone(as illustrated in Fig. 1), which is parallel with that of released acetaldehyde and the consumption of acetone. (as shown in Fig. 1)

It should be noted that all the concentrations of acetone scaled on the plot are initial concentration. (e.g. before irradiated)

The present results are consistent with many of the features of the mechanism proposed for the radiolysis of liquid ethanol by Wu^[9]. The following is just a refinement of their established mechanism which is relying on the present results and consideration of the yields of the new final products. (The square brackets indicate that the entities are within in spur.)

When γ -radiolysis upon liquid ethanol, following reactions occur initially.



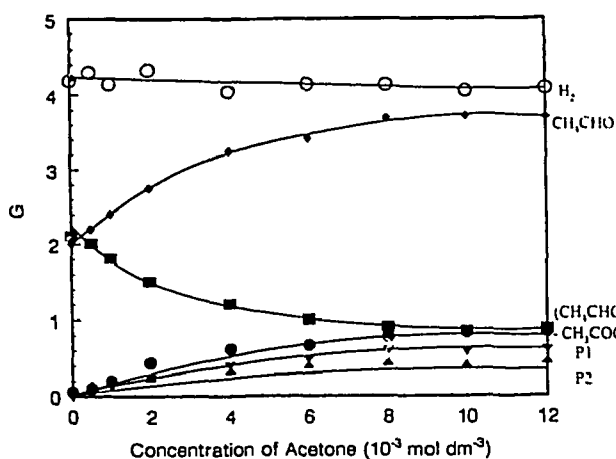
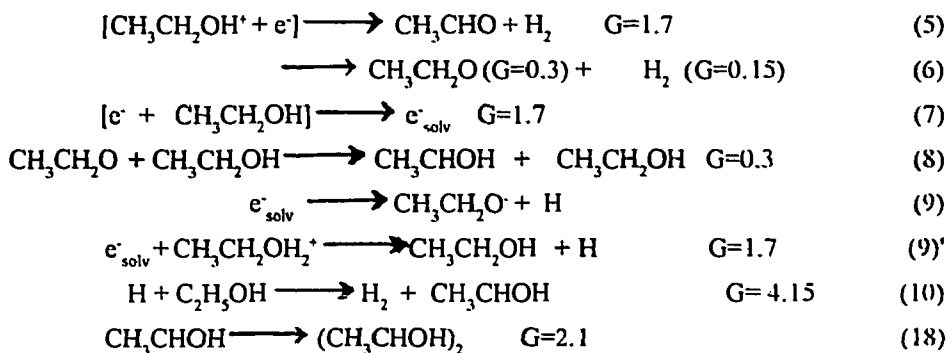
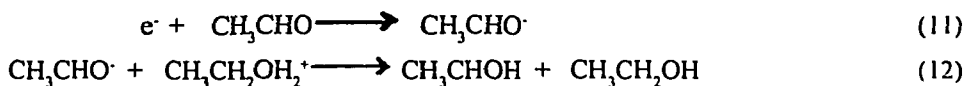
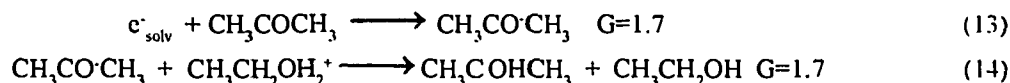


Fig. 1 The dependences of G values on acetone conc.; system saturated with N₂; dose rate:2Gy/s; dose:6000Gy

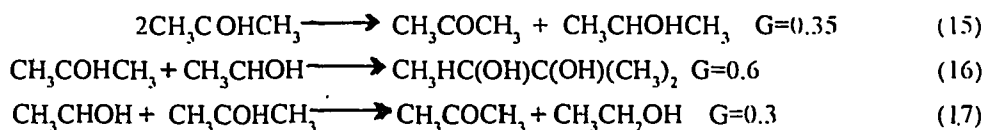
While absence of additives and dose > 160Gy, reactions(11) and(12) become important:



However, if acetone present as additive in this system, an alternative to reaction(10) as a fate for the solvated electrons e⁻_{solv} might be:



Thus, acetaldehyde is released. Then, what about the fate of CH₃COHCH₃ radical. Considering the new products, following reactions might occur:



Comparing the consumption of acetone and the redox potential of CH₃CHOH and CH₃COHCH₃ radical (E_{CH₃COHCH₃/CH₃COCH₃} = -1.3V, E_{CH₃CHOH/CH₃CH₂OH} = -1.1V), we could assume that reaction(17) may occur. According to the assumption mentioned above, it is reasonable to interpret the experimental result. In

the presence of acetone, hydrogen remains constant ($G(H_2) = 0.15 + 1.7 + 2.33 = 4.18$), because neither the reaction of H atom addition to acetone nor H abstraction from acetone occurs within the range of acetone concentration (up to $1.2 \times 10^{-2} \text{ mol dm}^{-3}$). The $G(\text{CH}_3\text{CHO})$ value rises significantly with increasing acetone concentration, which demonstrates definitely that acetone competes to capture the e_{solv}^- with acetaldehyde [reactions (11) and (13)]. When acetone captures all of the e_{solv}^- of the system, acetaldehyde is released to reach finally the limiting value $3.7 (G(\text{CH}_3\text{CHO}) = 2.0 + 1.7 = 3.7)$ accompanying by the formation of CH_3COCH_2 anion radical ($G=1.7$). Neutralization reaction of CH_3COCH_2 anion radical and $\text{CH}_3\text{CH}_2\text{OH}_2^+$ forms $\text{CH}_3\text{COHCH}_3$ radical ($G=1.7$) [reaction (14)] subsequently. From the G values of final products, considering the assumed way of disappearance of $\text{CH}_3\text{COHCH}_3$ radicals, the consuming yield of $\text{CH}_3\text{COHCH}_3$ radical ($G = 0.3 + 0.6 + 0.35 \times 2 = 1.6$) is obtained, which is agreement with the forming yield of CH_3COCH_2 anion radical. On the other hand, the yield of $(\text{CH}_3\text{CHOH})_2$ measured is also coincident with the yield of CH_3CHOH radical. In other words, a material balance between intermediates and final products of this system is obtained. From the discussion above, it seems that there is some correlation between disproportionation and the number of β hydrogen atom possessed by alcohol radicals. The more β hydrogen atoms a radical owns, the easier the disproportionation occurs.

According to the suggested mechanism, kinetic analysis of the data is studied, and following equations are given by:

$$d[e_{\text{solv}}^-]/dt = k_1 D - k_{11}[e_{\text{solv}}^-][\text{CH}_3\text{CHO}] - k_{13}[e_{\text{solv}}^-][\text{CH}_3\text{COCH}_3] \quad (1)$$

$$d[\text{CH}_3\text{CHO}]/dt = k_u D - k_{11}[e_{\text{solv}}^-][\text{CH}_3\text{CHO}] \quad (2)$$

D is the dose rate, k_1 and k_u are the rate constant of producing e_{solv}^- and acetaldehyde respectively. reaction (9) and neutralization reaction (9)' are neglecting when acetone ($10^{-3} \text{ mol dm}^{-3}$) presents.

When the steady-state has been established, $d[e_{\text{solv}}^-]/dt = 0$, so:

$$[e_{\text{solv}}^-] = kD / (k_{11}[\text{CH}_3\text{CHO}] + k_{13}[\text{CH}_3\text{COCH}_3]) \quad (3)$$

Thus an integrating equation is obtained⁽¹³⁾:

$$[\text{CH}_3\text{CHO}] / 2 - 1.7k_{13}[\text{CH}_3\text{COCH}_3] / 4k_{11} \times \ln(1 + 2k_{11}[\text{CH}_3\text{CHO}] / 3.7k_{13}[\text{CH}_3\text{COCH}_3]) = kD \quad (4)$$

D is the dose, and k is an conversion coefficient ($k = 1.3 \times 10^{-23}$).

Substituting the data of curve $G(\text{CH}_3\text{CHO})$ against concentrations of acetone in Fig. 1 into equation (4), one can obtain the ratio of rate constant against every experimental acetone concentration. It is apparent that the ratio varies at low concentration due to the assumption that $[\text{CH}_3\text{COCH}_3]$ remains constant during irradiation which is far deviating from the actual process. While at high concentration, the consumption of acetone can be neglected contrasting to its initial concentration, thus a constant approaching to 1 is obtained which is well fitted the steady state processing. When requiring a procedure depending on computer, $k(e_{\text{solv}}^- + \text{CH}_3\text{CHO}) / k(e_{\text{solv}}^- + \text{CH}_3\text{COCH}_3) = 0.96$ is achieved by simulation which is coincident with the value obtained by pulse radiolysis experiment. (Tab. 1)

Tab. 1 The ratio(k) of rate constants $k(e_{\text{solv}}^- + \text{CH}_3\text{CHO}) / k(e_{\text{solv}}^- + \text{CH}_3\text{COCH}_3)$ obtained from different methods

Conc.	Low ($< 4 \times 10^{-3} \text{ mol dm}^{-3}$)	High ($> 4 \times 10^{-3} \text{ mol dm}^{-3}$)
Steady State Application	Variations (5.0 - 1.5)	Approach to the Constant 1
Computer Simulation	0.96	0.96
Pulse Radiolysis	0.84	0.84

From the discussion above, we may be able to explain the discrepancy between the calculated value(k)

of Zhang's and that from pulse radiolysis. Being the simplest ketone, acetone is an easily volatile reagent. It is largely consumed when degassed, therefore, the $[CH_3COCH_3]$ should be redetermined after degassed but Zhang neglects this effect. On the other hand, it will lead to a great error at low acetone concentration supposing that $[CH_3COCH_3]$ keeps constant.

The results obtained in acetone ethanol system demonstrate the effect of carbonyl group to scavenge solvated electrons in irradiated ethanol solution resembles that in aqueous solution. Thus, we could employ ethanol as solvent probe to study other ketone compounds, especially some hydrophobic aromatic carbonyl compounds.

II. THE γ -RADIOLYSIS AND PULSE RADIOLYSIS OF ACETOPHENONE-ETHANOL SYSTEM

Acetophenone, an important aromatic carbonyl compound, reveals great importance in biological reaction, especially in electron transfer and oxidative phosphorylation. A lot of experiments have been done^[14,15,16], however, most of the studies carried out previously in the literatures investigated the reaction of solvated electron with acetophenone generally in aqueous solutions. Actually, acetophenone is less soluble in water which means the system studied has to be confined to a low acetophenone concentration. It is difficult to observe the effect of acetophenone on the intermediates as a function of concentration. On the other hand, the techniques often used are pulse radiolysis and flash photolysis, little has been done to study the products with γ -radiolysis in irradiated ethanol solution, in which acetophenone is easily soluble. Thus, there are still many disputations about the absorption spectra of the transient species. In course of this work, both γ -radiolysis method and pulse radiolysis are performed, the results are well agreement.

When γ -radiolysis acted upon acetophenone-ethanol solutions, the dependences of G values of the final products on acetophenone concentration were obtained. (as shown in Fig. 2)

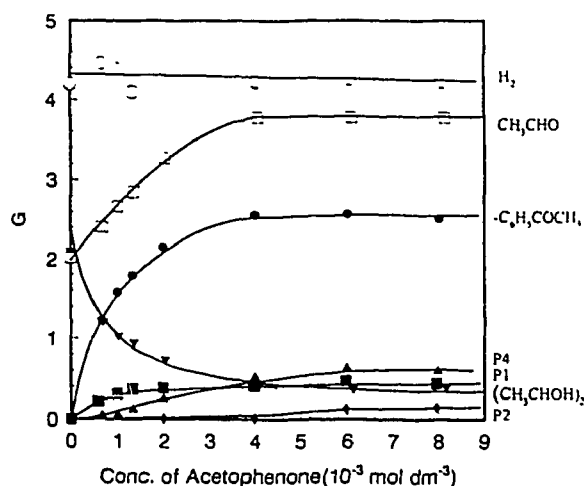


Fig. 2 The dependences of G values on acetophenone concentration. system saturated with N_2 ; dose rate 2.0Gy/s; dose:3000Gy

It is found that when increasing acetophenone concentration, the $G(H_2)$ values remain unchangeable. In contrast the $G(CH_3CHO)$ values rise significantly and the $G((CH_3CHO)_2)$ values decrease rapidly in this range of acetophenone concentration. It indicates that acetophenone being an effective e^-_{solv} scavenger like acetone, competes to capture the e^-_{solv} with acetaldehyde which is formed in γ -radiolysis of ethanol. [reactions (11), (19)]



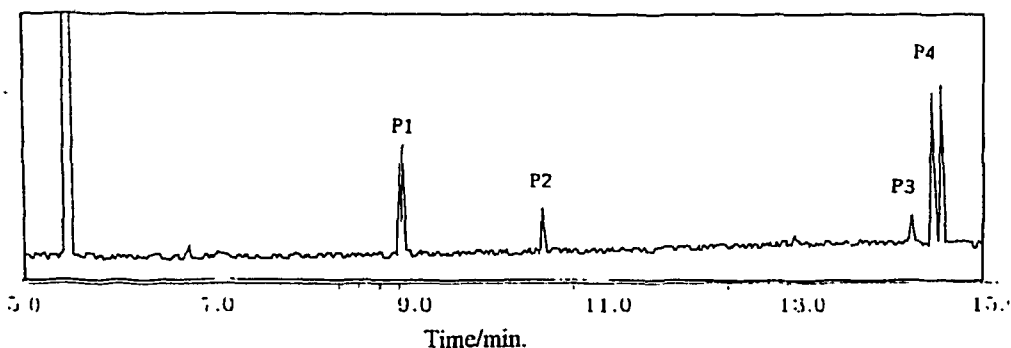


Fig. 3 GC-spectrum of the new final products in irradiated acetophenone ethanol solution (FID); 25m OV-1 capillary column; [acetophenone]=6.12mM; dose rate:2.0Gy/s, Dose:3000Gy

P1, P2, P3 and P4 are the four new final products, and are detected by GC-MS (see Fig. 3) and their structure are also determined. (see Fig. 4). Estimating calibration factors from those of other compounds with similar structure are used to calculate the G values of the new final products and the trends of the G values with increasing acetophenone concentration are illustrated in Fig. 2.

Considering the behaviour of the intermediates in acetone-ethanol system and the formation of the new final products of this system, following reactions may occur :

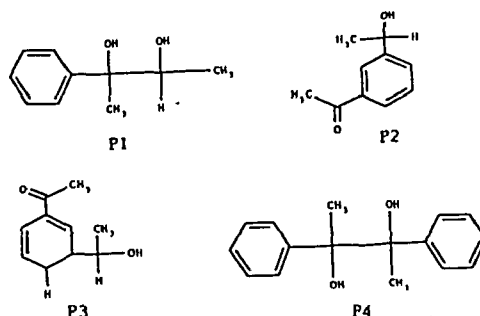
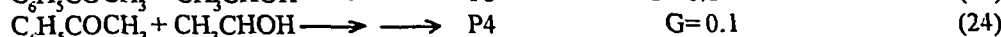
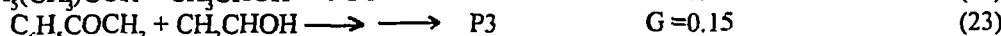
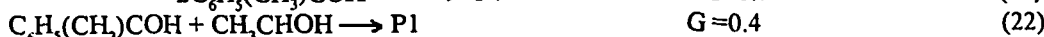
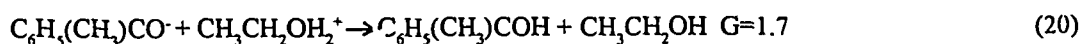


Fig. 4 The structures obtained four final products P1, P2, P3 and P4 respectively on GC detecting sequence

It is obvious that acetophenone can scavenge all the e^-_{solv} ($G=1.7$) to form ketyl radical ion $\text{C}_6\text{H}_5\text{CO}^\cdot\text{CH}_3$ and subsequently produce ketyl radical $\text{C}_6\text{H}_5\text{COHCH}_3$ ($G=1.7$). On the other hand, the obtained values of $G_{\text{P1}}=0.4$ and $G_{\text{P4}}=0.6$ reveal that recombination reaction takes place both between $\text{C}_6\text{H}_5\text{COHCH}_3$ ketyl radicals and hydroxyethyl radical ($G=0.4$) and among $\text{C}_6\text{H}_5\text{COHCH}_3$ radicals ($G=0.6 \times 2 = 1.2$). Meanwhile, the total consumption of $\text{C}_6\text{H}_5\text{COHCH}_3$ ($G=1.6$) to form P1 and P4 is obtained, which is coincident with the loss of e^-_{solv} ($G=1.7$) captured by acetophenone. In other words, a good material balance between e^-_{solv} and radiolytic products P1 and P4 is obtained. However, there is still uncertain about the way of producing P2 and P3, maybe they are formed via the disproportionation reaction of $(\text{CH}_3\text{CHOH})\text{C}_6\text{H}_5\text{COCH}_3$ radical.

From the discussion above, one can find that there are almost no disproportionation reaction occurs among ketyl radicals ($\text{C}_6\text{H}_5\text{COHCH}_3$), only recombination reaction exists between CH_3CHOH radical and ketyl radicals. On the other hand, it should be noted that the material balance is still unresolved in this system as a whole and the fate of a part of the loss of the acetophenone ($G=0.5$) and CH_3CHOH radical ($G=1.1$) is

unknown. Relating to the fact that CH_3CHOH radical can be added to the solutes in irradiated garlic-ethanol^[17] and baicalin system^[18], we could suppose that the adduct of two CH_3CHOH radical added to benzene ring of acetophenone might be formed.

The result of pulse radiolysis experiment (see Fig. 5 and 6) is another evidence to support the suggestion that acetophenone is an effective electron scavenger. The absorption spectra is characterized with absorption peaks at $\lambda_{\text{max}}=315\text{nm}$ and 440nm , both peaks decay unimolecularly with the same observed rate constant of $1.9 \times 10^5 \text{ s}^{-1}$. When N_2O saturated acetophenone ethanol was pulsed, no obvious absorption can be observed in the wavelength range used (300-750nm). Therefore, the optical spectra presenting on pulse radiolysis of Ar degassed acetophenone ethanol solution might be assigned to one species, an electron adduct of acetophenone. The 440nm peaks is well-known and has been ascribed to ketyl radical ion $\text{C}_6\text{H}_5\text{CO}^-\cdot\text{CH}_3$ in previous literature. Thus, one might postulate that an electron charge transfer from the carbonyl group to the benzene ring might exist as following:

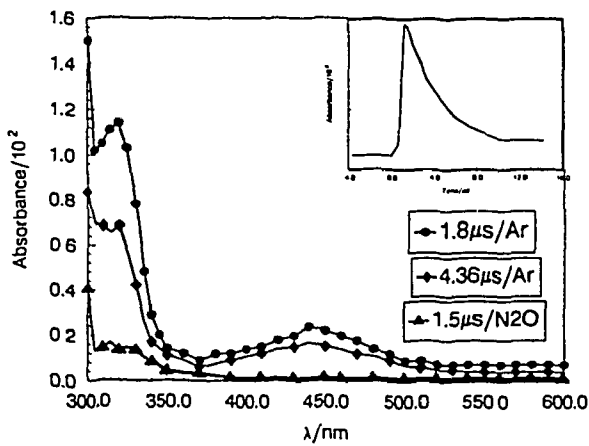
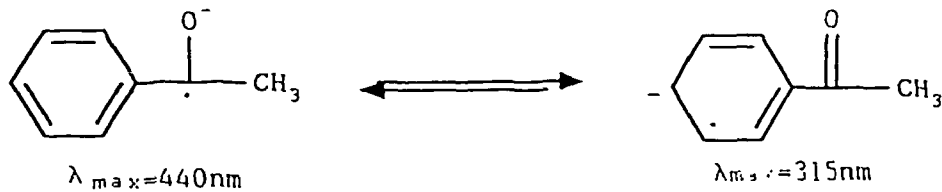


Fig.5 Transient spectra of Ar(N_2O) saturated acetophenone ethanol solution (1mM, neutral); insert: absorbance decay at 310nm; pulse dose: 1Gy

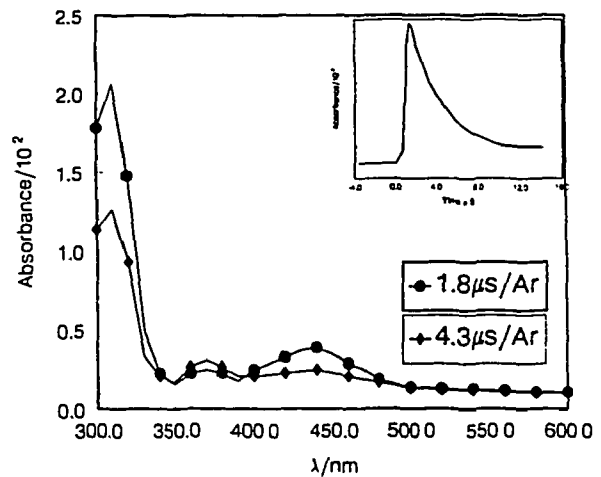


Fig. 6 Transient spectra of Ar saturated acetophenone aqueous solution (2mM, 0.2M t-BuOH, PH 6.5); insert: absorbance decay at 440nm, dose: 1Gy

The species with $\lambda_{\text{max}}=315\text{nm}$ and $\lambda_{\text{max}}=440\text{nm}$ might decay by ethanolysis. Electron adducts of arene are known to hydrolysis to form cyclohexadienyl radicals, thus one might assume that the electron adducts of acetophenone could ethanolysis and a pseudo first order decay could be observed.

In addition, comparing Fig. 3 and Fig. 4, we may can infer that ethanol can act as a more convenient solvent than water when applied in pulse radiolysis owing to there is less disturbance of extra additives which is often introduced in water solution. One can get a more direct observation of transient species in ethanol solution.

Using the previously determined data in γ -radiolysis experiment, according to the differential equations (5,6) given, taking $k_{18}/k_8=4$, one can get the simulation curve of $G(\text{CH}_3\text{CHO})$ varying with the concentration of acetophenone (see Fig. 7)

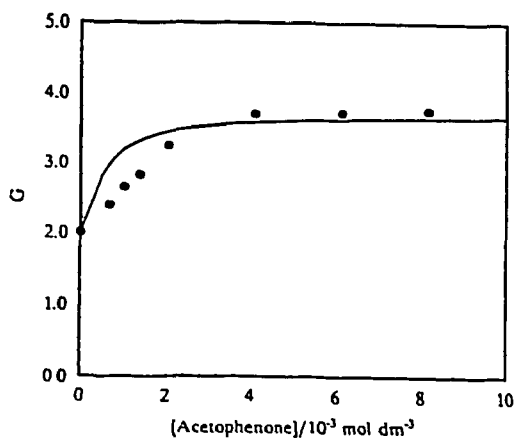


Fig. 7 The simulation curve for acetophenone competing the solvated electrons with acetaldehyde

$$d[e^-_{solv}]/dt = k_1 D - k_{11}[e^-_{solv}][CH_3CHO] - k_{19}[e^-_{solv}][C_6H_5COCH_3] \quad (5)$$

$$d[CH_3CHO]/dt = k_2 D - k_{11}[e^-_{solv}][CH_3CHO] \quad (6)$$

Comparing the structures of acetophenone and flavonoids such as baicalin, (see Fig.8) one can find that the A ring combining a carbonyl group of C ring in baicalin is similar to acetophenone. As a whole, baicalin combines a much greater conjugation system than that of acetophenone and demonstrates dominant difference of scavenging effect contrasting to acetophenone. Acetophenone can effectively scavenge e^-_{solv} produced in liquid ethanol while baicalin can't. (see Fig.9). We may draw a conclusion that the larger conjugation structure in baicalin far weakens the character of the carbonyl group function and makes baicalin difficult to capture the electron, which is vital in human body and does not disturb the normal electron transferring in body when baicalin is used as medicine. From the discussion above, we could find that the curing effect of flavonoids acting as medicine is really closely related to their possessing big conjugation system.

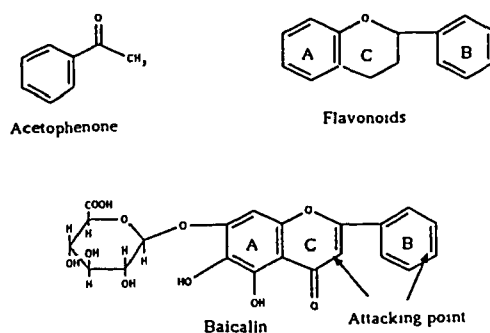


Fig. 8 Comparison of the structures of acetophenone, flavonoids and baicalin

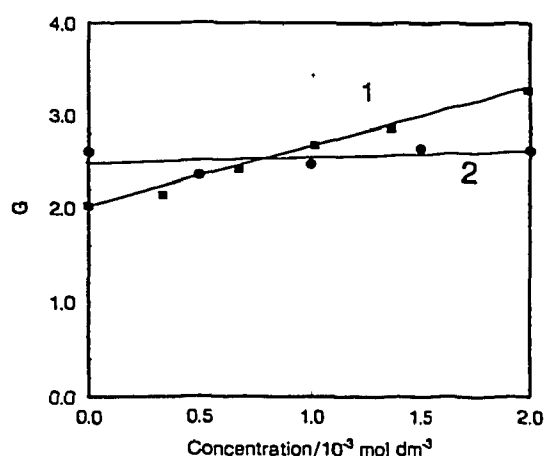


Fig. 9 The dependences of acetaldehyde G values on additives concentration.
 1: acetophenone ethanol solution; dose rate: 2.0Gy/s; dose: 3000Gy
 2: baicalin ethanol solution; dose rate: 0.5Gy/s; dose: 969Gy.

SUMMARY

In this paper:

(1) A good material balance between intermediates and final products in acetone ethanol solution was obtained, which demonstrate that some products in ethanol solution might be predicted. The achieved ratio of rate constant $k(e^-_{\text{soliv}} + \text{CH}_3\text{CHO})/k(e^-_{\text{soliv}} + \text{CH}_3\text{COCH}_3) = 0.96$ is well agreement with that of pulse radiolysis, which indicates that we can employ ethanol as a solvent probe to study the chemical behaviour of carbonyl group of ketone compounds.

(2) Both γ -radiolysis and pulse radiolysis of acetophenone ethanol solution confirm that acetophenone id an effective electron scavenger and there might be electron adducts isomers, both of them decays at the same rate constant via ethanolysising.

(3) Relating to the behaviour of CH_3CHOH radical in aqueous solution and liquid ethanol^[13] as well as that of other kinds of alcohol radicals in ethanol solutions, one can find that different medium will affect the behaviour of alcohol radical. For example CH_3CHOH radical can undergo both recombination and disproportionation reaction at the almost same rate in aqueous ethanol, but very few disproportionation reaction of CH_3CHOH radical are observed in the radiolysis of liquid ethanol. At the same time, it seems that the number of β hydrogen atom belonging to the alcohol radical also takes an important role in disproportionation reaction. (see Tab.2), the more β hydrogen atoms a radical owns, the easier the disproportionation occurs.

Tab. 2 The influence of the number of β hydrogen atoms on reaction types

Radicals	CH_3CHOH	$(\text{CH}_2)_2\text{COH}$	$\text{C}_6\text{H}_5(\text{CH}_2)\text{COH}$
Number of β H Atoms	3	6	3
Reactions Type	R	D	R

R: Standing for Recombination Reaction

D: Standing for Disproportionation Reaction

References:

1. A. O. Allen, The Radiation Chemistry of Water and Aqueous Solutions. Van Norstrand. Princeton. NJ, 1961

2. R. S. Dixon, *Radiat. Res. Rev.*, 2, 237(1970)
3. A. J. Swallow, A. B. Ross and W. P. Helman, *Radiat. Phys. Chem.*, 17, 127(1981)
4. Zhang N., Wu J. L., *Radiat. Phys. Chem.*, 38, 383(1991)
5. Asmus K. D., Warman J. M. and Schuler R. H. J. *Phys. Chem.*, 74, 246(1970)
6. Spinks J. W. T. and Woods R. T. (1990) *An Introduction to Radiation Chemistry*
7. Bolton G. L. and Freeman G. R., *J. Am. Chem. Soc.*, 98, 6825(1976)
8. Mahan Y and Freeman G. R., *J. Phys. Chem.*, 89, 4347(1985)
9. Wu J. L. and Zhang X. J., Report on the 4th Japan-China Bilateral Symposium on Radiation Chemistry. 55 pp.
10. Mahan Y. and Freeman G. R. *J. Phys. Chem.*, 91, 1561(1987)
11. Wei G. S and Wu J. L. et al, *Chemical Journal of Chinese Universities*, 13, 1109(1992)
12. Zhang X. J., Wu J. L., Ha H. F., *Acta Physico Chimica Sinica*, 6, 298(1990)
13. Zhang X. J., Wu J. L., Zhou Y. R., *Radiat. Phys. Chem.*, 43, 335(1994)
14. A. G. Pribush and S.A. Brusnetseva, *Radiat. Phys. Chem.*, 16, 277(1980)
15. Hayon, T. Ibata, N.N. Lictin and M. Simic, *J. Phys. Chem.*, 76, 2072(1972)
16. D. W. Willans, *Radiat. Phys. Chem.*, 10, 335(1977)
17. Wang. G.H., Ph. D. Thesis of Peking University(1994)
18. Cai Z. L., Ph. D. Thesis of Peking University(1993)
19. von Sonntag, C., Schuchmann, H.-P. In *Oxygen Radicals in Biological System, Part C., Methods in Enzymology*, vol.233; Packer, L., Ed.; Academic Press: Orlando, FL, 1994, p3