

Basic medium oxidation of aromatic α -hydroxy-ketones: A free radical mechanism

Virginia Gómez-Vidales^a, Marina Vargas^a, Iván Meléndez^a, Manuel Salmón^{a,*}, Carmen Sansón-O^b, I.P. Zaragoza^c, Mikhail Zolotukhin^c, Roberto Salcedo^{c,*}

^a Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 México, D.F., Mexico

^b Facultad de Química, Universidad Nacional Autónoma de México, Circuito Escolar, s/n, Ciudad Universitaria, Coyoacán, C.P. 04510 México, D.F., Mexico

^c Instituto de Investigación en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04510 México, D.F., Mexico

ARTICLE INFO

Article history:

Received 18 May 2009

Received in revised form 12 October 2009

Accepted 14 October 2009

Available online 21 October 2009

Keywords:

Electron paramagnetic resonance (EPR)

Free radical

Benzoin

Theoretical study

ABSTRACT

A systematic study was undertaken of the EPR of sodium hydroxide solutions of Benzoin, Anisoin and Thenoin in both ethanol and DMSO as well as their corresponding ionised species of varying colours. In all cases, the EPR consist of symmetric spectra, resulting from the generation of a free radical-anion. Furthermore, theoretical DFT methods were applied in order to study the radical anions, revealing the reason for the colour change in the solutions and in the case of benzoin, found to be related to the interaction between the *cis* and *trans*-isomers with the molecules in the two solvents. We have defined the structure of the *cis*-isomer and for the first time we have described how the adduct between the *cis*-isomer and the solvent molecule, results in a stable conformer. This corresponds with the EPR results which indicated a significant difference between the *cis* and *trans*-isomers. Both the theoretical and experimental results inspired similar descriptions of the significant differences between the *cis* and *trans*-isomers in solution.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Benzoin and similar molecules are able to participate easily in an oxidation process which yields the so-called free radical benzyl. This process, previously studied by Iwaizumi and Abe [1] was further extensively analysed because the reactions display very peculiar behaviour, depending on the environment where this oxidation occurs. For the first time, Ihring and Caldwell [2] confirmed the formation of the free radical in the reaction solution; a result which had been described 19 years earlier [3].

Each reaction solution easily developed a colourful environment in a basic medium, either blue where the solvent is DMSO, or purple if the reaction is performed in ethanol; however, the coloured product is very labile and degrades rapidly [1,4].

This peculiar phenomenon has inspired many different explanations; Ihring and Caldwell [2] suggested that the product was a semiquinone and Michaelis and Fetcher [3] proposed that the colour was due to the presence of molecular oxygen dissolved in the solution. On the other hand, Iwaizumi and Abe [1], with results based on visible and EPR spectroscopy, proposed that the explanation for the coloured product lay in the formation of symmetric species containing a radical-anion such as the one represented in Figs. 1 and 2; these being resonant structures of the same species.

EPR and its corresponding theoretical simulation have been shown to be very useful tools for the characterization of free radical anionic species [5,6] and have been similarly applied in this work. Russell [5] has carried out extensive investigations concerning semidione ions and their isomers. One of his studies [5a] concerns a case similar to that presented in the present paper, where he and his co-workers studied an aliphatic semidione, with an equilibrium similar to that manifested by aromatic diketone and offered an explanation based on ion-pairing. Our discussion of benzoin complements and extends this work by Russell.

One of the main purposes of this communication is to validate the suggestion made by Iwaizumi and Abe by carrying out an EPR study, and also by applying theoretical calculations. We also attempt to provide an explanation for the varying colours of the solutions, depending on the solvents employed. Thus we conducted similar EPR experiments on benzoin and other related molecules. Besides this, the above experimental work was corroborated by means UV and IR spectroscopy and applying (Density Functional Theory) DFT calculations, together with the corresponding spectra simulation.

2. Materials and methods

The EPR measurements of the benzoin were made on a flat cell at room temperature, with a Jeol JES-TE300 spectrometer operating at X-Band mode, at a modulation frequency of 100 kHz. The

* Corresponding authors. Tel.: +52 55 5622 4600; fax: +52 55 5616 1201 (R. Salcedo).

E-mail address: salcedo@servidor.unam.mx (R. Salcedo).

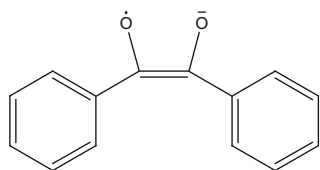


Fig. 1. Radical-anion **a** suggested by Iwazumi and Abe [1].

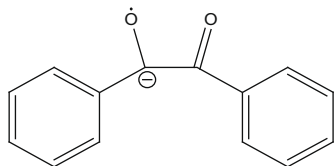


Fig. 2. Alternative radical-anion **a1**.

spectra were simulated using the program ESPRIT-382, v1.916. Each EPR spectra was recorded as a first derivative and the main parameters, such as the g -factor values and the hfcc (hyperfine coupling constants) were calculated according to Weil et al. [7].

All the α -hydroxy-ketones were studied in both Ethanol and DMSO solution. Some of these solutions displayed colour when NaOH 0.5 M was added, whereas others manifested no change. Therefore, a solution of each sample was placed on a flat cell in order to acquire and study the EPR spectra of each radical-anion formation *in situ* and the observed results are summarized in Table 1. Subsequently, the visible region spectra were recorded in a spectrophotometer UV–visible UNICAM UV 500 Thermo Spectronic, with Software Vision 32; for both freshly prepared and concentrated solutions of benzoin in (a) EtOH and (b) DMSO (0.2 mg/ml), each containing a small amount of NaOH 0.5 M (these displayed blue and purple colours, respectively).

Besides this, all the structures were theoretically optimized in the gas phase using a Jaguar 4.0 package [8]. For the purpose of energy evaluations, a pure DFT (Density Functional Theory) method was applied, which included Becke's gradient correction [9] for exchange and Perdew–Wang's for correlation [10]. The entire calculation was performed using the 6-31G** basis set. Gaussian time-dependent calculations [11], taking into account the EtOH and DMSO environments were performed on the conformational isomers of the benzoin radical-anion species, in this case employ-

ing the B3LYP method [9,10] with the aug-cc-pVDZ basis set [12]. This method was applied in order to provide an explanation for the colour change taking place in the different solutions. Additionally, NWChem calculations [13] were carried out in order to establish the possible types of interactions occurring between the benzoin conformers and the solvents. The theoretical UV and IR spectra were obtained from the same TD results and from frequencies calculations on the optimized structures of the *cis* and *trans*-isomers.

3. Results and discussion

The reactions in either basic/ethanol or basic/DMSO solution proceeded as shown in Fig. 3.

The oxidation mechanism involves the loss of two hydrogen atoms; the first generates the anion and the second the free radical. This needs to be a synchronized process between the lost hydrogen atom from the hydroxyl group and the hydrogen attached to the carbon atom that originally supported the hydroxyl group (see Fig. 3). The same kind of experiment was carried out for the different species, as shown in Fig. 4. From this it is evident that in all cases, the resulting species developed a free radical-anion, corresponding to a doublet state.

Thus, by using the EPR spectroscopy and the DFT calculations, we were able to establish and confirm the proposal made by Iwazumi and Abe [1]. The EPR spectrum corresponding to the benzoin sample solution (a), in DMSO/NaOH exhibited a very stable and intense blue-coloured, free radical with an isotropic signal, containing hyperfine coupling interactions centred at $g = 2.0057$, corresponding to a typical organic free radical and surely indicating a doublet state. The hyperfine coupling constant (hfcc) values for these signals were; $a_H = 0.107$ mT for 2 H, $a_H = 0.101$ mT for 4 H and $a_H = 0.037$ mT for 4 H, with a line width of $\Delta H_{p-p} = 0.016$ mT. Likewise, the spectra for benzoin in both EtOH and DMSO were theoretically calculated and are shown in Fig. 5.

The EPR spectrum of the anisoin sample in ethanol (**b'**) showed a very stable purple coloured free radical, with an isotropic signal centred at $g = 2.0055$, assigned to a free organic radical. The hfcc values for these signals were $a_H = 0.010$ mT for 6 H corresponding to the methyl protons, at $a_H = 0.106$ mT for 4 H and $a_H = 0.042$ mT for 4 H, with a line width of $\Delta H_{p-p} = 0.028$ mT. Besides in this case, the theoretical values for all of these data were also calculated from the simulated spectra. The epr spectra manifest a clear difference for benzoin in either DMSO or Ethanol solution, in terms of line width.

Table 1

Comparison of the hfcc of the free radical formed by α -hydroxy-ketones. The theoretical calculations has been made without dissolvent effect.

Compound	g -value	Line width ΔH_{p-p} (mT)	Hfcc (mT) calculated by simulation	Hfcc theoretical
Benzoin/DMSO a	2.0057	0.016	0.107 (2 H), 0.101 (4 H), 0.037 (4 H)	0.160 (2 H), 0.125 (4 H), 0.044 (4 H)
Benzoin/EtOH b'	2.0055	0.028	0.107 (2 H), 0.101 (4 H), 0.042 (4 H)	
Anisoin/DMSO b	2.0056	0.010	0.010 (6 H), 0.106 (4 H), 0.037 (4 H)	0.010 (6 H), 0.127 (4 H), 0.042 (4 H)
Anisoin/EtOH b'	2.0055	0.010	0.010 (6 H), 0.106 (4 H), 0.039 (4 H)	
Thenoin/DMSO c	2.0055	0.012	0.207 (2 H), 0.166 (2 H), 0.040 (2 H)	0.272 (2 H), 0.241 (2 H), 0.063 (2 H)
Thenoin/EtOH c'	2.0055	0.012	0.229 (2 H), 0.184 (2 H), 0.041 (2 H)	

The hfcc values reported by Strom has been made in DMSO–*t*BuOH (80–20%) [5].

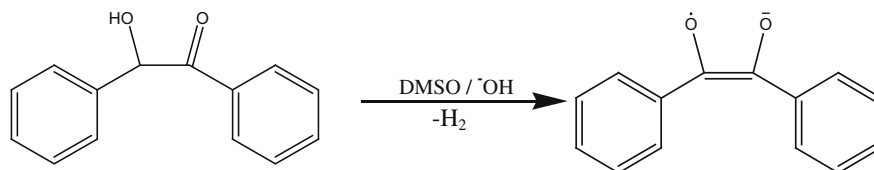


Fig. 3. Reaction of benzoin in alkaline DMSO solution.

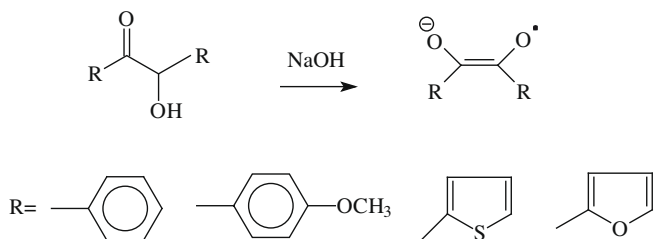


Fig. 4. The general reaction was made in both, DMSO and EtOH as solvents.

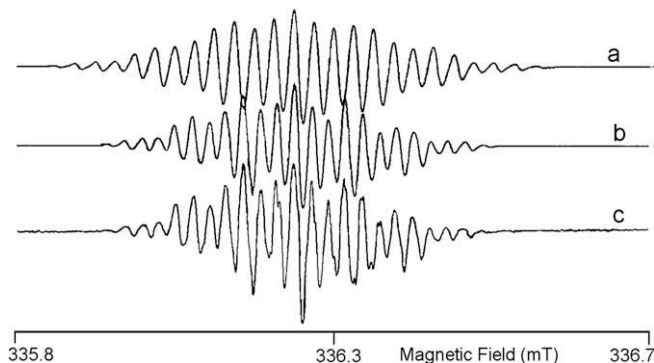


Fig. 5. EPR spectra of benzoin in DMSO solution (a) theoretical spectra, (b) simulated spectra and (c) experimental spectra.

The thenoin EPR spectrum (c') in ethanol/NaOH displayed a very stable and green coloured free radical, with an isotropic signal centred at $g = 2.0055$. The hfcc values were $a_H = 0.229$ mT for 2 H, $a_H = 0.184$ mT for 2 H, and $a_H = 0.041$ mT for 2 H.

The compounds (b)–(d) exhibited free radicals in DMSO, and in all cases manifested small gross changes in terms of their signal peaks, as well as in their hfcc. The above technique was also used to obtain the EPR spectra of the reaction products for the compounds in DMSO/NaOH, and associated hfcc values.

The assignation of the peaks in all the experimental spectra appears to be similar to that suggested by Russell [5]. We have a doublet signal generated by the loss of a hydrogen atom which generates a free radical, strongly influenced by the negative charge that arises when the other hydrogen atom is released in the form of a proton. Russell suggested the presence of two species in the solution of semidiones in the presence of K^+ , these species are precisely the conformational ions *cis* and *trans* that inspired this discussion, based on the experimental results we have described and the theoretical discussion which follows.

Extensive interpretation of the experimental EPR spectra has been undertaken, corroborated by theoretical calculations and this is currently an important topic [14]. Previously, a simple method was suggested for the comparison of experimental and theoretical EPR spectra [14]. This method can be applied in a straightforward way to our study. The experimental, simulated and theoretical spectra of benzoin, anisoin and thenoin are all shown in Figs. 5–7. The simulated, theoretical and experimental results are presented in Table 1. A qualitative match between the three types of data can be clearly observed. Although the quantitative match is not exact; the global result led us to the conclusion that the generation of the charge, as well as the formation of the free radical corresponds to that described by Iwaizumi and Abe [1], especially as these calculations were performed on the species specifically suggested by these authors.

Based on the above comparison, we propose that the theoretical method can be used to follow the pathway of the active species formation. The molecular modelling studies were carried out using

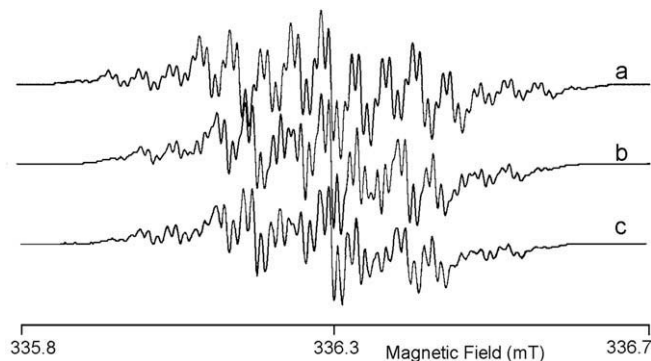


Fig. 6. EPR spectra of anisoin in ethanol solution (a) theoretical spectra, (b) simulated spectra and (c) experimental spectra.

DFT methods, which confirmed the source and sequence of free radical formation during the oxidation of a and b. This technique allowed us to establish the following sequence: (1) the free radical a is formed by the loss of the hydrogen atom, which is linked to the carbon atom that supports the hydroxyl group (Fig. 1). This conclusion was reached by comparing the radical generated by the previously mentioned hydrogen loss and the free radical obtained when the hydrogen atom was lost from the hydroxyl group (Fig. 2). The radicals manifested a clear difference in energy level of 1.483 eV, favouring the first case. Planarity of the aromatic moiety with the free radical permits electronic delocalisation, increasing the stability of these intermediates. (2) The process outlined above is followed by the loss of the hydrogen atom that belongs to the hydroxyl group as a proton. Thus the final product is a radical-anion where delocalisation can be found on both the negative charge and the free electron and this species yields a doublet which is also responsible for the complexity of the EPR signal.

The proposal that both electronic configurations are delocalized is upheld by analysis of the frontier molecular orbitals. The unrestricted calculation of the radical-anion species yielded a result in which the α and β HOMO's have eigenvalues of 0.1088 and 2.2041 eV, respectively. The first of these is a SOMO (single occupied molecular orbital) and the second is a virtual LUMO. The shape of these regions is shown in Fig. 8.

Both orbitals are practically equal and obviously belong to the same irreducible representation. Therefore, the actual nature of the SOMO was approximated by carrying out an open-restricted calculation.

The shape of this last orbital is practically the same as those shown in Fig. 8, however this orbital is localized halfway between the α and β orbitals, with an eigenvalue of 0.789 eV. It is possible to observe that both the free electron and the negative charge have

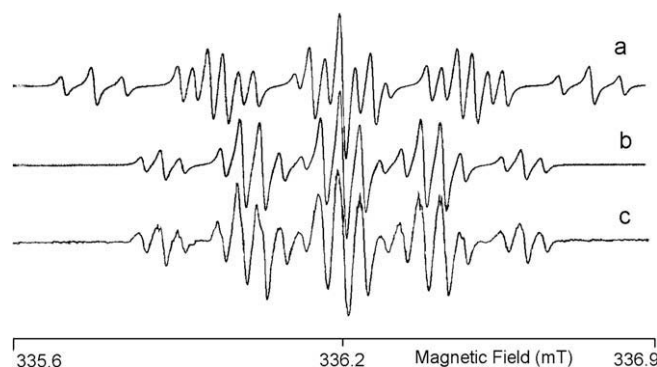


Fig. 7. EPR spectra of thenoin in ethanol solution (a) theoretical spectra, (b) simulated spectra and (c) experimental spectra.

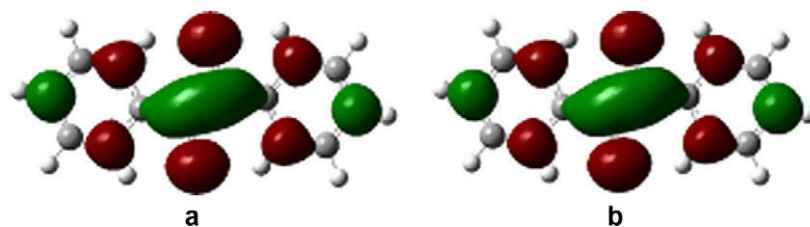


Fig. 8. Shape of molecular orbitals: (a) SOMO; (b) LUMO.

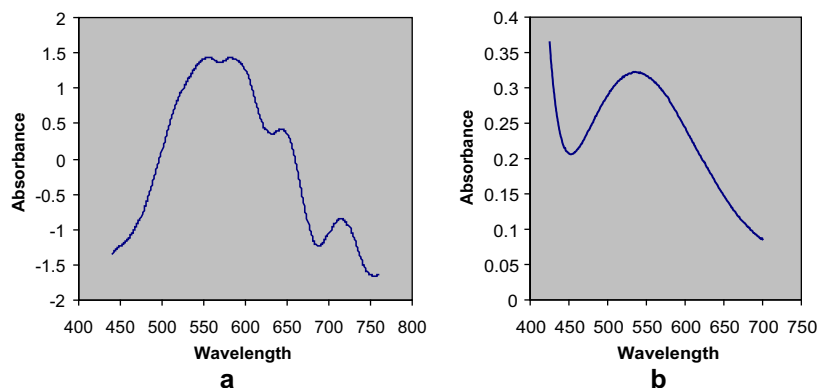


Fig. 9. Comparison between theoretical absorption bands and experimental spectra of solutions of benzoin: (a) visible spectrum in DMSO; (b) visible spectrum in EtOH.

access to a large region within this orbital. Again, it is this delocalisation which causes the complexity of the EPR spectrum.

However, the most important challenge is to answer the essential question; how are the various observed behaviours, related to the solvent? Further calculations were made, considering the solvent in a time-dependent approximation [11] in order to simulate the electronic spectra of the benzoin molecule. Thus, all the visible spectra of the conformational isomers *cis* and *trans* were simulated in the context of EtOH and DMSO environments. When comparing the experimental visible spectra with the theoretical simulations, the results are very interesting, revealing that the *isomer trans* of the free radical-anion species is the only conformer present in EtOH solution, however the *isomer cis* of the same radical-anion is present in significant quantities in the DMSO solution. These differences give rise to the different colours observed in the solutions. The experimental spectra and the corresponding values for the electronic transitions obtained from the theoretical calculations are shown in Fig. 9 and table 2, respectively. The strong band at 550 nm of the *isomer trans* is the only important absorption in the EtOH solution, whereas the two sets of bands from both isomers are mixed in the

Table 2
Theoretical absorption bands for both isomers in DMSO and EtOH.

Isomer <i>cis</i> /DMSO	719
	555
	498
Isomer <i>trans</i> /DMSO	600
	595
	437
Isomer <i>cis</i> /EtOH	706
	512
	485
Isomer <i>trans</i> /EtOH	584
	566
	422

corresponding spectrum from the DMSO solution; these consisting of the two bands at 570 and 582 nm from the *trans*-isomer and the 710 nm band from the *isomer cis*.

This phenomenon was confirmed by an infrared study. Both colored solutions were analysed by IR spectroscopy and the results were compared with theoretical calculations of frequencies that were carried out in order to get the corresponding theoretical spectra. It is important to emphasize three features; first, the calculations were carried out on the species that contains two carbonyl groups, this is little different to the commercial benzoin in which there are a hydroxyl and a carbonyl group. Second, for the same reason, we have a situation of two isomers (*cis* and *trans*) and the calculations were carried out for each isomer, therefore we have two different spectra for the same chemical specie, obviously in practice this would be different because a sample of benzoin would have no isomers or in case of having two carbonyl groups would content both isomers. Third, the experimental spectra were recorded in presence of the solvents (that are the majority of the samples) DMSO and ethanol with the basic medium, therefore they retain the signals corresponding to these solvents in spite of the subtraction of the computer, however the spectra are useful and it is possible to appreciate the important bands for the present study.

The theoretical spectrum of the *cis*-isomer show two own important bands, the one at 1215 cm^{-1} that corresponds to the bending of the carbon-carbon bond that supports both carbonyl groups and the one at 1407 cm^{-1} which corresponds to the asymmetric stretching of both carbonyl groups. These bands can also be insight in the experimental spectra recorded in basic medium of DMSO (1208.5 and 1408, respectively), this comparison is shown in Fig. 10a.

In the case of the *trans*-isomer, the theoretical spectra shows the same band corresponding to the bending of the same C-C bond, but it appear at 1091 cm^{-1} whereas the asymmetric stretching of the carbonyl groups appear at 1360 cm^{-1} . These bands also appear in the experimental spectra recorded in basic medium of EtOH

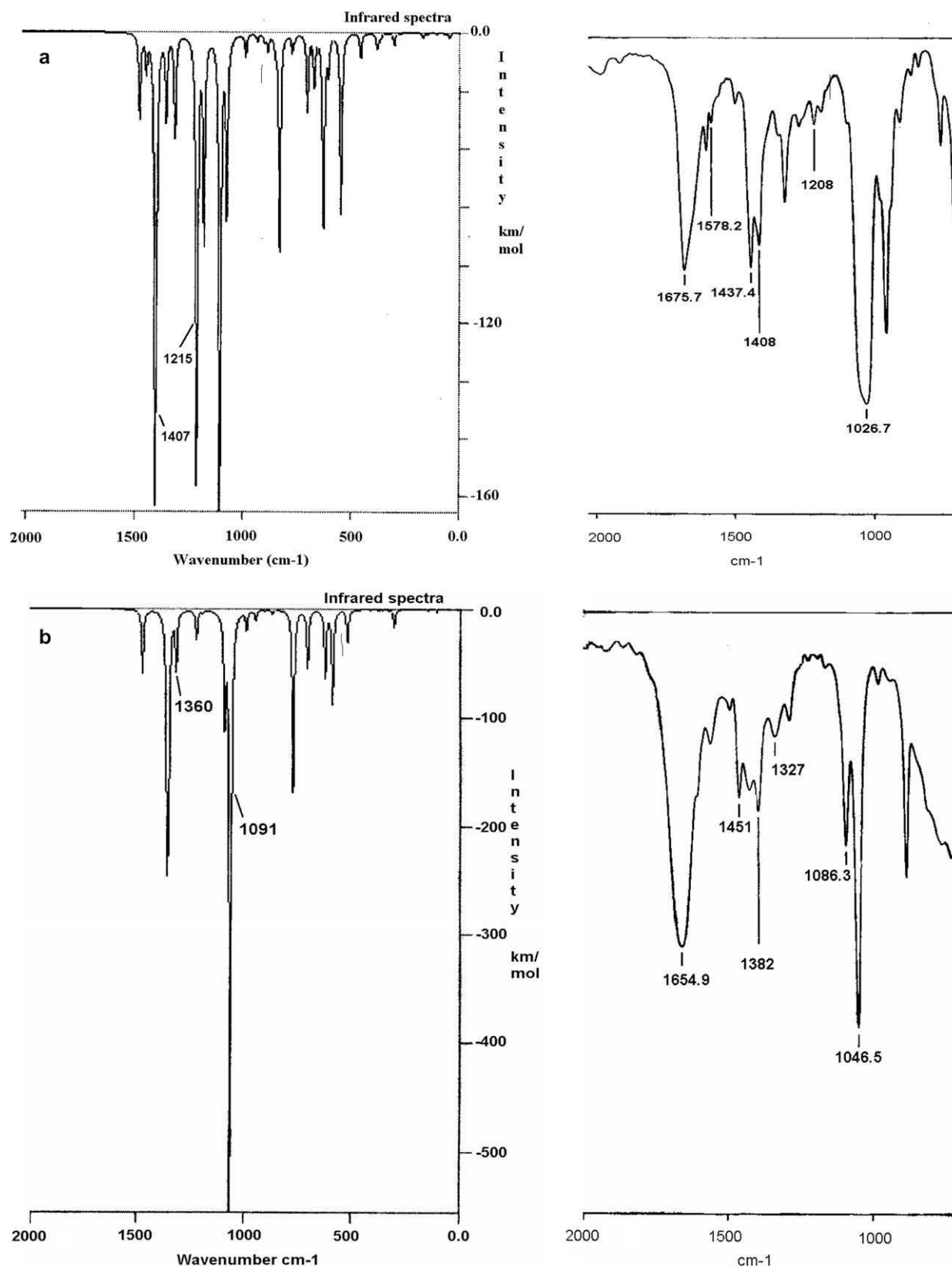


Fig. 10. (a) Theoretical IR spectrum of the *cis*-isomer compared with experimental IR spectrum from benzoin obtained in basic médium of DMSO. (b) Comparison between theoretical IR spectrum of the *trans*-isomer and the experimental IR spectrum of benzoin achieved in basic médium of EtOH.

(1102 and 1382 cm^{-1}) and as weak shoulders in the basic médium of DMSO spectra, this comparison is shown in Fig. 10b. The important point is that the *trans*-isomer appear as a majority species (al-

most unique) in the EtOH médium whereas *cis*-isomer has important presence in the basic médium DMSO spectrum which is the same behaviour predicted by the UV-visible studium.

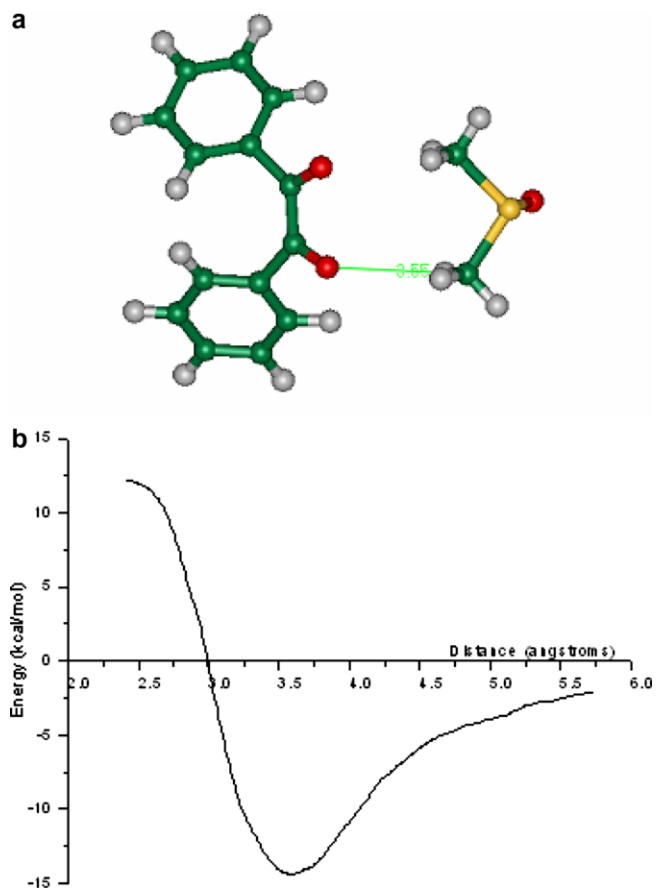


Fig. 11. (a) Schematic representation of the interaction between the free radical-anion of benzoin and the DMSO molecule; (b) energy plot for the interaction shown in (a).

It is important to note that the quantitative differences in the delocalization of these two isomers may relate to the fact that the optimization of the geometry of the *trans*-isomer yields a totally planar species, whereas the corresponding geometry of the *cis*-isomer manifests a deviation from planarity, due to the steric hindrance that arises between the hydrogen atoms substituted on both aromatic rings. Thus the *trans* species should be more stable than the *cis*, owing to its improved resonance framework.

The peculiar, contrasting behaviour observed for both isomers in the two solutions may be explained as follows: the *trans*-isomer represents the most stable of the two and is the main species present in EtOH solutions, whereas the *cis*-isomer is the dominating presence in the DMSO solution, where the DMSO molecule interacts directly with the benzoin radical-anion, by means of two hydrogen bridges which are able to fix the *cis* conformation position. A NWChem dynamic calculation [12] of both species revealed this kind of interaction, both molecules are positioned in a free space and brought together. Where the interaction is successful, a bond will occur, but where no interaction occurs, the molecules will rebound. As a result, an attraction effect arises due to the coupling phenomenon (see Fig. 11a). This effect is evident, if the energy is plotted versus the distance between the oxygen atoms of benzoin and the hydrogen atoms of the methyl fragments of DMSO (see Fig. 11b). An energy minimum at 3.55 Å indicates that hydrogen bridges have been formed.

Free radicals are responsible for the signals found in the visible spectra (and also for the EPR signals). However, fresh experiments were carried out in order to investigate the presence of these free radicals. Following the technique proposed by Nuñez-Vergara et al. [15], oxygen was bubbled into the flasks of both the EtOH and the DMSO solutions of benzoin (containing a small quantity of NaOH solution) and the colour quickly disappeared in both cases. Thus, when the visible and epr spectra of both clear solutions were recorded, no signal appeared. Oxygen reacts with the free radicals, following the pathway presented here:

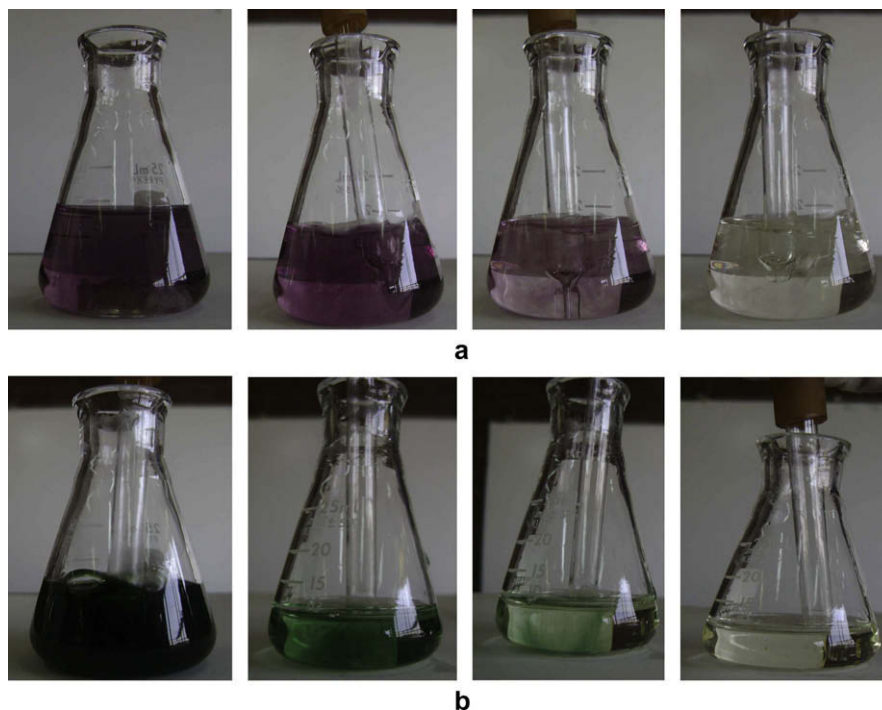
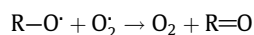


Fig. 12. Reaction of benzoin and oxygen in basic medium (a) In EtOH; (b) In DMSO.

The reaction was photographed in order to show how the process occur and the colour is lacked in both cases. These images can be seen in Fig. 12.

Similar behaviour was found in the other species, but the case of benzoin is the clearest, therefore this was used as the general example.

4. Conclusions

When the EPR spectra of certain aromatic α -hydroxy-ketones were studied, the spectra as well as the theoretical calculations confirmed that the signal corresponds to a doublet induced by an anionic free radical which arises from the loss of two hydrogen atoms, one from the carbon chain that supports the hydroxyl group and the other from the hydroxyl group. This phenomenon was clearly confirmed by calculations indicating the nature of the SOMO, generated by the loss of these atoms. The nature of the visible spectra was explained by means of time-dependent theoretical calculations, which indicated that the solution of benzoin in EtOH contained only the *trans*-isomer of the radical-anion. However, the same solute in DMSO resulted in significant amounts of both the *cis* and the *trans*-isomers. Likewise, the relationship between free radical species and the different spectra was demonstrated by the reaction of the free radical and oxygen with an associated lack of colour and signals, in the corresponding spectra.

Acknowledgements

The authors wish to gratefully acknowledge, to Mr. Marco A. Salcedo, Ms. Maria Teresa Vázquez, Ms. Oralia Jimenez, Ms. Sara Jimenez and Mr. Victor Gomez for technical help, the authors also are indebt with DGSCA-UNAM and Sun Enterprise for invaluable help in computation work. This research was supported by projects PUNTA-UNAM, CONACYT-59935 and CONACYT-57432.

References

- [1] T. Abe, M. Iwaizumi, Bull. Chem. Soc. Jpn. 47 (1974) 2593.
- [2] J.L. Ihring, R.G. Caldwell, J. Am. Chem. Soc. 78 (1956) 2097.
- [3] L. Michaelis, E.S. Fetcher Jr., J. Am. Chem. Soc. 59 (1937) 1246.
- [4] W. Kawai, Kagaku 23 (1953) 363.
- [5] (a) G.A. Russell, C.E. Osuch, J. Am. Chem. Soc., 104 (1982) 3353–3358 (and references therein);
(b) E.T. Stromm, G.A. Russell, J.H. Schoeb, J. Am. Chem. Soc. 88 (1966) 2004–2007.
- [6] S. Ralhan, P.K. Shukla, N.K. Ray, Ind. J. Chem. A, Inorg., Bioinorg., Phys., Theor. Analyt. Chem., 42A (2003) 2493–2495.
- [7] J.A. Weil, J.R. Bolton, J.E. Wertz, Electron Spin Resonance. Elementary Theory and Practical Applications, J. Wiley and Sons, New York, 1994.
- [8] Jaguar 4.0, Schrödinger, Inc., Portland, OR, 1991–2000.
- [9] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [10] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseira, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millarn, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslovski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian03, Gaussian Inc., Wallingford, CT, 2004.
- [12] (a) T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007–1023;
(b) D.B. Woon, T.H. Dunning Jr., J. Chem. Phys. 103 (1995) 4572–4585.
- [13] E.J. Bylaska, W.A. de Jong, K. Kowalski, T.P. Straatsma, M. Valiev, D. Wang, E. Apra, T.L. Windus, S. Hirata, M.T. Hackler, Y. Zhao, P.-D. Fan, R.J. Harrison, M. Dupuis, D.M.A. Smith, J. Nieplocha, V. Tipparaju, M. Krishnan, A.A. Auer, M. Nooijen, E. Brown, G. Cisneros, G.I. Fann, H. Fruchtl, J. Garza, K. Hirao, R. Kendall, J.A. Nichols, K. Tsemekhman, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsels, M. Deegan, K. Dyall, D. Elwood, E. Glendenning, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, L. Pollack, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, A. Wong, Z. Zhang, NWChem, A Computational Chemistry Package for Parallel Computers, Version 5.0, Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA, 2006.
- [14] M. Shiotani, P. Persson, S. Lunell, A. Lund, F. Williams, J. Phys. Chem. A 110 (2006) 6307–6323.
- [15] L. Nuñez-Vergara, J.A. Squella, C. Olea-Azar, P.A. Navarrete-Encinas, J.C. Strum, Electrochem. Acta 45 (2000) 3555–3561.