Cis \rightleftharpoons Trans Photoisomerization of Azobenzene–Cyclodextrin Inclusion Complexes[†]

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trans- and cis-azobenzene form with α -, β -, and γ -cyclodextrin inclusion complexes which can be evidenced by UV and induced circular dichroism spectra. The inclusion in the cyclodextrin cavity has different consequences on the photoreactivity of the two isomers. The reactivity of the cis isomer is practically unaffected while the photoisomerization quantum yields of the trans isomer are strongly reduced with respect to the aqueous medium; moreover, the wavelength dependence of the yields tends to vanish. A partial or total block of the torsional motion about the -N=N- double bond and the inversion at one of the nitrogens as sole isomerization coordinate are the most likely rationalization of the experimental findings.

Introduction

Cyclodextrins (CDx) are cyclic oligosaccharides composed of six (or more) D(+)-glucopyranose units linked by an α -(1,4) glycosidic linkage. Cyclodextrins with 6, 7, and 8 glucose units are called α -, β -, and γ -cyclodextrins, respectively. Each CDx has a toroidal, hollow shape whose internal diameter is, approximately, 5 (α -CDx), 7 (β -CDx), and 9 Å (γ -CDx) and whose depth is 7 Å.¹⁻³ The spatial arrangement of functional groups in CDx molecules results in a variety of interesting features of these compounds. Primary and secondary hydroxyl groups are located at the narrower and wider rims of the torus, respectively: so the exterior of the molecule is relatively hydrophilic. The interior of the torus consists of a ring of C-H groups, a ring of glucosidic oxygens, and another ring of C-H groups; therefore, the interior of CDx's is relatively hydrophobic.

The most important property of CDx's is their ability to admit a variety of appropriately sized guest molecules into the cavity with formation of inclusion complexes. The recognized potential of the CDx-guest interaction as a model for enzyme active sites has attracted the attention of many investigators.^{1,4,5} Moreover, the photophysical and photochemical properties of organic molecules included in the cyclodextrin cavity are, also, largely different from those of the molecules in aqueous solution. Fluorescence intensity enhancement,⁶⁻⁸ intra-⁹⁻¹¹ and intermolecular^{12,13} excimer formation, intramolecular exciplex emission,¹⁴ room-temperature phosphorescence emission,¹⁵⁻¹⁷ change in the rate of proton dissociation,¹⁸ and changes in proton-induced excited-state quenching¹⁹ have been reported to occur in solution in the presence of CDx. Moreover, the products distribution for the photo-Fries rearrangement of esters^{20,21} and amides²² is different in the presence and absence of β -CDx and the photodimerization of water-soluble anthracene derivatives is greatly enhanced in the presence of γ -CDx.²³

In this paper we studied the cis \Rightarrow trans photoisomerization of azobenzene aqueous solutions in the presence of α -, β -, and γ -CDx. The main feature of this photoreaction in homogeneous solution is a marked wavelength effect on the quantum yields for the trans \rightarrow cis photoprocess following excitation in the S₁ (n, π^*) or S₂ (π,π^*) band. This behavior²⁴ has been attributed to the existence of two different isomerization coordinates involving the twisting around the -N=N- double bond or the in-plane inversion at one of the two nitrogen atoms. The torsional mode is active only when the molecule is excited in S_2 whereas the inversion is operative in S_1 .²⁵⁻²⁷ According to Rau,²⁵⁻²⁷ the isomerization in S₂ occurs via a rotational mechanism, while according to Monti et al.,²⁶ the decay of S_2 occurs through two routes: one leading to S_1 , the only excited state from which isomerization ensues, and the second leading directly to S_{0} without producing isomerization. Both these suggestions are in agreement with the experimental finding that the geometrical photoisomerization of two azobenzophanes²⁵ and an azobenzene capped crown ether,²⁷ molecules

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The aim of the work was to study the photochemical behavior of azobenzene-cyclodextrin inclusion complexes and, in particular, to verify whether the encapsulation of azobenzene in the cavity constitutes a constraint strong enough to block some of its molecular motions.

Experimental Section

trans- and cis-azobenzene were the same as used in previous work.^{24,28} Cyclodextrins were Aldrich products used as received. The light source was a stabilized high-pressure mercury lamp (Osram HBO, 200 W) coupled with a high-intensity Bausch & Lomb grating monochromator (1350 grooves/mm; blazed at 300 nm), with slits of 2 mm (entrance) and 1.5 mm (exit). Ferrioxalate actinometry²⁹ was used. Trans \rightleftharpoons cis photoisomerization yields

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for which rotation is hindered for structural reasons, does not show any wavelength effect on the isomerization quantum yield.^{25,27}

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Figure 1. Absorption spectra of *trans*-azobenzene: (--) in tetrahydrofuran; (---) in H₂O/CH₃OH (80/20 v/v); (---) in 10⁻² M α -CDx aqueous solution (see Experimental Section) ([trans] = 5 × 10⁻⁵ M; π,π^* band, cell path 1 cm; n, π^* band, cell path 2 cm).

were measured by irradiating thoroughly stirred air-equilibrated solutions of the cis or trans isomer: $[\text{trans}] = 5 \times 10^{-5} \text{ M}$ and $[cis] = 1.5 \times 10^{-4} \text{ M};$ cell thickness was 1-4 cm according to the irradiation wavelength and the isomer under study. The solutions of azobenzene + 10^{-2} M CDx were prepared starting from a concentrated methanol solution of azobenzene diluted 1:100 with aqueous solutions of CDx to carry out the experiments; the 10^{-2} M CDx solutions so contain 1% MeOH, by volume. The fraction of the light transmitted at the irradiation wavelength was taken into account. Conversion percentages were determined by UV spectrophotometry in the region 310-350 nm directly on the irradiated solution in 0.5-1-cm-thick cells. For irradiations at 313 nm maximum conversion percentages were 10% for the trans \rightarrow cis process and 2% for the cis \rightarrow trans one; for irradiations at 436 nm, the conversion percentage was $\sim 10\%$. A double-beam Perkin-Elmer 320 spectrophotometer was used. Induced circular dichroism spectra were obtained by a Jasco J 500 dichrograph.

Results and Discussion

Figure 1 shows the absorption spectrum of trans-azobenzene in water/methanol (80/20 v/v), water + 10^{-2} M α -CDx, and tetrahydrofuran, a low-polarity ($\epsilon = 7.58^{30}$) solvent which mimics the interior of a cyclodextrin cavity. On going from the aqueous medium to water plus 10^{-2} M α -CDx, a red shift of both the π,π^* (from 320 to 325 nm) and the n,π^* (from 425 to 440-2 nm) absorption λ_{max} is observed. The integrated molar absorption of the π,π^* band is similar in water and in α -CDx solution while the value of the n, π^* band in H₂O is about 2 times that in 10⁻² M α -CDx. The differences between tetrahydrofuran and the CDx solution are, instead, more pronounced for the π , π^* than for the n, π^* band. In 10⁻² M β -CDx and in aqueous medium the S₂ band of trans-azobenzene practically superimposes; the intensity of the S_1 band, instead, is about 2/3 that of the band in H_2O/C_2H_5OH ; moreover, the λ_{max} is shifted from 425 to 435 nm. In 10⁻² M γ -CDx no reliable information on the intensity of the two bands could be obtained owing to the formation of a precipitate. By operating in 1 M NaOH solutions of cyclodextrin, no precipitation occurs and no variation with respect to the aqueous medium could be observed in the spectrum; however, in this case, a modification of the γ -CDx dimensions due to partial salification of the hydroxyl groups cannot be excluded. The UV-vis spectral variations point out the formation of an inclusion complex between α - and β -CDx (the host) and trans-azobenzene; the variations themselves cannot be described in terms of the polarity of the microenvironment in which the guest azobenzene lies. In fact, the red shift of the n,π^* band in the presence of 10^{-2} M α -CDx, with respect to the aqueous



Figure 2. n, π^* absorption band of *trans*-azobenzene in the presence of various amounts of α -CDx: (---) H₂O/CH₃OH (80/20 v/v); [α -CDx] = (1) 1.5 × 10⁻⁴ M; (2) 3 × 10⁻⁴ M; (3) 5 × 10⁻⁴ M; (4) 10⁻³ M; (5) 3 × 10⁻³ M; (6) 10⁻² M ([*trans*-azobenzene] = 5 × 10⁻⁵ M; cell path 2 cm).

solution, is not accompanied by a blue shift of the π,π^* band (see, for comparison, the spectrum in tetrahydrofuran).

None of the CDx's affect the absorption spectrum of *cis*-azobenzene. So, for *cis*-azobenzene, like for the system *trans*-azobenzene plus γ -CDx, no evidence of inclusion complex formation can be obtained from UV spectral data, as reported in ref 31; however, for the above systems, clear evidence for the formation of inclusion complexes could be obtained from induced circular dichroism spectra (see later).

Figure 2 shows the effect on the S_1 band of *trans*-azobenzene caused by the addition of increasing amounts of α -CDx; there is not a regular decrease of the optical density with the increasing concentration of α -CDx which can be taken as an indication that the stoichiometry of the complex is not 1:1. This is confirmed by the variations of the S_2 band, not reported for sake of clarity, in which the spectra of the solutions containing intermediate amounts of cyclodextrin do not cross at 328-329 nm, the isosbestic point of the aqueous and 10^{-2} M α -CDx solutions. The band decreases in intensity on going from the aqueous medium to 5 \times 10^{-3} M α -CDx solutions; for higher concentrations the intensity of the band increases again. The formation of complexes with stoichiometry different from 1:1 has already been reported for complexes between CDx's and organic molecules.^{32,33} In particular, it has been shown that the α -CDx-methyl orange complex has a 2:1 stoichiometry both in solution, at a CDx concentration higher than 5×10^{-3} M,³⁴ and in the crystalline state.³⁵

Circular Dichroism Studies. The formation of inclusion complexes between azobenzene and CDx's is confirmed by induced circular dichroism (icd) spectra. Figures 3 and 4 show icd in the absorption region of isomeric azobenzenes when included in the cavity of CDx's. The trans isomer with the three cyclodextrins shows a positive band in the region of the S₂ absorption (250–350 nm) while in the region of the S₁ absorption (350–550 nm) it shows a negative band with α - and β -CDx and a positive band with γ -CDx. The cis isomer gives in all cases similar signals, positive

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Figure 3. Icd spectra of 5×10^{-5} trans-azobenzene aqueous solutions in the presence of (--) 10^{-2} M α -CDx, (---) 10^{-2} M β -CDx, and (---) 10^{-2} M γ -CDx (region 259-360 nm, cell path 2 cm; region 360-550 nm, cell path 10 cm).



Figure 4. Icd spectra of 1.7×10^{-4} M cis-azobenzene aqueous solutions in the presence of (---) 10^{-2} M α -CDx, (---) 10^{-2} M β -CDx, and (---) 10^{-2} M γ -CDx (cell path 2 cm).

in the π,π^* and negative in the n,π^* absorption regions. The presence of Cotton effects with the cis isomer supports the inclusion of the molecule in the cyclodextrin cavity, in disagreement with the conclusions drawn in ref 31 on the basis of the influence of CDx's on the absorption spectrum. The results suggest that the inclusion complexes of *trans*-azobenzene with α - and β -CDx have similar structures; the azo dye is included axially in the cavity of cyclodextrins. It has been shown, in fact, that the sign of icd is determined, for aromatic-CDx complexes, by the orientation of the transition dipole moments of the guest molecule with respect to the axis of the cavity.³⁶ A positive value of the icd signal is produced by transitions whose polarization is parallel to the long axis of CDx, while a negative signal is produced by those polarized perpendicularly. In trans-azobenzene, the π,π^* band is largely due to a transition polarized in the plane, along the long axis of the molecule, ^{37,38} while the n, π^* could have out-of-plane polarization components due to nonplanarity of the molecule.³⁹ The axial inclusion of *trans*-azobenzene in the α - and β -CDx cavity is confirmed by the crystalline structure of α -CDx-methyl orange inclusion complex.³⁵ Complexation with γ -CDx seems to involve a different geometry which could be related to the possibility that one γ -CDx molecule includes in its large cavity more than one

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Figure 5. Icd spectra of the *cis*-azobenzene- β -CDx complex in the presence of various amounts of Me₂SO: (1) 1%; (2) 3%; (3) 10%; (4) 15%; (5) 20%; (6) 30% by volume. [cis] = 2 × 10⁻⁴ M; [β -CDx] = 10⁻² M; cell path 2 cm.

molecule of *trans*-azobenzene.⁴⁰⁻⁴² In this respect, experimental suggestion for the inclusion by CDx or more molecular species has been obtained by icd spectra of *cis*-azobenzene + 10^{-2} M β -CDx in the presence of different amounts of dimethyl sulfoxide (Me₂SO) reported in Figure 5, In 10^{-2} M β -CDx, *cis*-azobenzene exhibits, besides a positive band a 290 nm, a negative band at 410 nm. By addition of increasing amounts of Me₂SO, a new band, positive in sign, with maximum at 450 nm, is developed; its intensity increases with increasing concentration of Me₂SO up to 20% Me_2SO (by volume). For higher concentrations of Me_2SO the intensity of the band at 450 nm decreases, and for Me₂SO concentrations higher than 50% by volume no icd signal is observed at all in both the absorption regions. This is in agreement with the findings of ref 43, in which the dissociation constants of aromatic $-\beta$ -CDx complexes are reported to be 2 orders of magnitude higher in Me₂SO than in aqueous medium. This behavior can be rationalized in terms of a progressive inclusion of Me₂SO molecules in the cavity already occupied by *cis*-azobenzene. This inclusion should modify the interaction of cis-azobenzene with the interior wall of the cavity either by a sort of complexation of Me₂SO with the azo compound or, simply, by occupancy of a part of the interior of the cavity. A complexation between Me₂SO and β -CDx which could serve as a flexible capping for the entrapped azobenzene, as proposed for the system α -(1-naphthyl)ethylamine- β -CDx in Me₂SO/H₂O (60/40),⁴⁴ cannot be excluded, but it does not explain the absence of icd signals in mixtures $H_2O/$ Me_2SO with Me_2SO content >50%.

For *cis*-azobenzene, the sign of icd signals is similar to those of *trans*-azobenzene; however, due to the strongly nonplanar structure of the molecule, it is difficult to infer the geometry of the inclusion.

The Benesi-Hildebrand treatment of the icd signals in the π,π^* and n,π^* regions of absorption for the system *trans*-azobenzene- β -CDx is shown in Figure 6. The different values of the intercept/slope ratio at the two analysis wavelengths suggest that the host and guest do not interact in the ratio 1:1.

 $Trans \rightleftharpoons Cis Photoisomerization$. The only detectable photochemical reaction of azobenzene-cyclodextrin inclusion complexes is the trans \rightleftharpoons cis photoisomerization, as shown by the

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Figure 6. Benesi-Hildebrand plot of the icd signal of 3.8×10^{-5} M trans-azobenzene aqueous solutions in the presence of various amounts of β -CDx: \Box , 310 nm; O, 435 nm.

TABLE I: Photoisomerization Quantum Yields^{*a*} for Azobenzene Irradiated in the π,π^* (313 nm) and in the n,π^* (436 nm) Absorption Band

	$\phi_{\rm c} \ ({\rm trans} \rightarrow {\rm cis})$		$\phi_t \text{ (cis} \rightarrow \text{trans)}$	
	313 nm	436 nm	313 nm	436 nm
H ₂ O/CH ₃ OH (80/20 v/v)	0.205	0.315	0.40	0.425
<i>n</i> -hexane	0.105	0.25	0.44	0.515
tetrahydrofuran	0.085	0.19	0.40	0.485
α -CDx (10 ⁻² M)	0.11	0.15	0.405	0.415
β -CDx (10 ⁻² M)	0.132	0.138	0.40	0.485
γ -CDx (10 ⁻² M)	-		0.40	0.46

^aAccuracy: ±7%.

changes of the absorption spectra with the irradiation time. In Figure 7 are reported, as an example, the spectral variations for the *trans*-azobenzene- α -CDx complex irradiated at 313 nm: the three isosbestic points, at 237, 284, and 375 nm, are maintained for irradiations prolonged far after the photostationary-state attainment.

The quantum yields of the trans \rightarrow cis (ϕ_c) and cis \rightarrow trans (ϕ_t) processes obtained by irradiation at 313 and 436 nm in various solvents and in water $+ 10^{-2}$ M cyclodextrins are collected in Table I. Significant variations are observed in the photochemical behavior of the trans isomer: both α - and β -CDx lower the quantum yield of the photoprocess, both irradiating in the π,π^* and in the n,π^* band. This effect could be ascribed, at least in part, to the quite apolar microenvironment of the cyclodextrin cavity; in fact, ϕ_c values in *n*-hexane and tetrahydrofuran are lower than the corresponding values in H_2O/CH_3OH . However, as already pointed out, the spectral variations in 10^{-2} M α -CDx cannot be interpreted uniquely on the basis of the medium polarity but indicate the formation of an inclusion complex. Therefore, a variation of the photoreactivity is likely. The most interesting feature is that no difference in the photochemical behavior of the two bands is observed in the presence of β -CDx and that the difference tends to vanish in the presence of α -CDx. The effect



Figure 7. Spectral variations of 5×10^{-5} M *trans*-azobenzene aqueous solutions in the presence of 10^{-2} M α -CDx, irradiated at 313 nm (cell path 1 cm).

of the inclusion is the same achieved by blocking by a cyclophane structure or with a crown ether the rotation about the -N=Ndouble bond, i.e. an equal value of the photoisomerization yield in the two bands, as reported by $Rau.^{25,27}$ Information about the structure of the inclusion complex would be of great aid in understanding if and what molecular motions are preferentially influenced by the complexation. It seems reasonable to assume that two cyclodextrins encapsulate the molecule of trans-azobenzene, as suggested by the UV and/or icd variations as a function of CDx concentration, and that the nitrogen atoms of the azo group are included and located at the neck of the cavity, as reported in the literature for the complex methyl orange- α -CDx^{34,35} The molecular motions in inclusion complexes are slowed down, as demonstrated by ²H and ¹³C nuclear relaxation studies of the systems methyl cinnamate- and *p*-tert-butylphenolate- α -CDx.45 In included trans-azobenzene, the torsional movement about the -N=N- double bond is expected to be much more hindered than the in-plane inversion. This latter requires, in fact, less room to be fulfilled and is, therefore, less influenced by the interaction with the microenvironment. As a consequence, the deactivation paths of the S_2 state, assisted by the rotation movement,²⁶ are unfavored with respect to the internal conversion $S_2 \dashrightarrow S_1$ and the wavelength effect on photoisomerization is suppressed.

The presence of the dextrins practically does not affect the ϕ_t at both irradiation wavelengths. The lack of effect could indicate a geometry of the complex *cis*-azobenzene-CDx different from that of the *trans*-azobenzene-CDx complex, i.e. a less deep inclusion in the cavity is likely for the cis isomer. In this case, large variations in photoreactivity are not expected because the excited states of the cis isomer have mixed n,π^* and π,π^* character²⁶ due to the large deviation from planarity of this compound. This mixing of the excited states is reflected by the small difference in the quantum yields of the photoisomerization process by irradiating in the S₁ or S₂ band; in various solvents, of different polarity, ϕ_t by irradiating in S₂ is ~0.4 and in S₁, 0.5.^{24c} Moreover, it must be mentioned that, according to Fischer and co-work-

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ers,^{46–48} a substantial increase of the medium viscosity obtained by cooling does not affect the quantum yields of the cis \rightarrow trans process while it strongly reduces the yields for the reverse reaction.

The present findings confirm that when rotation about the -N=N- double bond is hindered, the photochemistry of azobenzene from the first and the second excited singlet state is the same. If in homogeneous media the photoisomerization occurs exclusively via the inversion mechanism (as suggested by Monti et al.²⁶) or via the rotation and inversion, according to the excited

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state populated by light excitation (as suggested by $Rau^{25,27}$), is a question which, at the moment, remains unanswered.

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Registry No. α -CDx complex with *trans*-azobenzene, 109553-46-0; β -CDx complex with *trans*-azobenzene, 109553-47-1; γ -CDx complex with *trans*-azobenzene, 109553-48-2; α -CDx complex with *cis*-azobenzene, 109553-49-3; β -CDx complex with *cis*-azobenzene, 109553-50-6; γ -CDx complex with *cis*-azobenzene, 109553-51-7; azobenzene, 103-33-3; cyclodextrin, 12619-70-4.

Flash Photolysis Resonance Fluorescence Investigation of the Gas-Phase Reactions of OH Radicals with a Series of Aliphatic Ketones over the Temperature Range 240–440 K

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Absolute rate constants have been determined for the gas-phase reactions of OH radicals with a series of aliphatic ketones by the flash photolysis resonance fluorescence measurement technique. Experiments were performed over the temperature range 240-440 K at total pressures (using Ar diluent gas) between 25 and 50 Torr. The rate constant data for acetone (k_1) , 2-butanone (k_2) , and 3-pentanone (k_3) were used to derive the Arrhenius expressions $k_1 = (1.7 \pm 0.4) \times 10^{-12} \exp[-(600 \pm 75)/T]$ cm³ molecule⁻¹ s⁻¹, $k_2 = (2.3 \pm 1.1) \times 10^{-12} \exp[-(170 \pm 120)/T]$ cm³ molecule⁻¹ s⁻¹, and $k_3 = (2.8 \pm 0.3) \times 10^{-12} \exp[(10 \pm 35)/T]$ cm³ molecule⁻¹ s⁻¹. At 296 K, the measured rate constants (in units of 10^{-13} cm³ molecule⁻¹ s⁻¹) were $k_1 = 2.16 \pm 0.16$, $k_2 = 11.5 \pm 1.0$, and $k_3 = 27.4 \pm 1.3$. Room temperature rate constants for the reaction of OH radicals with a number of other 2-ketones were also determined. These were (in the above units) 3,3-dimethyl-2-butanone (12.1 ± 0.5), 2-pentanone (40.0 ± 2.9), 2-hexanone (66.4 ± 5.6), 2-heptanone (86.7 ± 8.4), 2-octanone (110 ± 9), 2-nonanone (122 ± 13), and 2-decanone (132 ± 12). The error limits represent 2 standard deviations (from the least-squares analysis); we estimate that an additional 5% uncertainty should be added to account for possible systematic error in the measurements. These results are discussed in terms of reactivity trends for C-H bonds located in the α , β , and γ positions with respect to the carbonyl group.

Introduction

The gas-phase reaction with hydroxyl (OH) radicals represents an important loss process for ketones in the earth's atmosphere.^{1,2} The need for a thorough understanding of the kinetics of these reactions is enhanced by the increased use of such oxygenates as fuel additives. Nevertheless, the extensive kinetic data base which exists for the reaction of OH radicals with many different classes of organic compounds³ does not extend to the reaction of OH radicals with ketones. More specifically, there are no studies on the temperature dependence of the rate constants; and multiple room temperature results exist only for acetone, 2-butanone, 4-methyl-2-pentanone, and 2,6-dimethyl-4-heptanone.⁴⁻¹¹ Furthermore, for acetone and 2-butanone significant discrepancies exist in the reported room temperature data.

We thus decided to conduct a systematic investigation of the kinetics of the reactions of OH radicals with series of ketones in order to resolve existing discrepancies in the literature and to provide a data base for the temperature dependence of these reactions. The kinetic measurement technique employed was flash photolysis resonance fluorescence (FPRF) at temperatures between 240 and 440 K and total pressures between 25 and 50 Torr (achieved with argon diluent). The results from these studies constitute the first measurements of the temperature dependence of the reactions of OH with acetone, 2-butanone, and 3-pentanone and the only existing rate constant measurements (at room temperature) for 2-heptanone, 2-octanone, 2-nonanone, 2-decanone, and 3,3-dimethyl-2-butanone. Our room temperature results for 2-pentanone and 2-hexanone are the first to be obtained by an absolute kinetic measurement technique. The series of 2-ketones was selected in order to develop a reactivity index (at 296 K) for C-H bonds positioned α , β , and γ to the carbonyl group of the ketone.

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