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Photochemistry of alkyl aryl ketones on alumina, silica-gel and water ice surfaces

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Dedicated to Prof. Dr. Jakob Wirz on the occasion of his 60th birthday

Abstract

Investigation of the Norrish type II photoreaction of alkyl aryl ketones on alumina, silica-gel, and water ice surfaces is reported. The reaction was studied in terms of the quantum efficiency and the photoproduct distribution as well as the influence of the reaction temperature. A model in which the short-lived biradical intermediate interacts with the surface, in addition to polar effect on the excited triplet of ketone, is proposed. An Application of alumina for microwave photochemical experiment is reported.

Keywords: Photochemistry; Microwave; Alkyl aryl ketones; Valerophenone; Alumina; Silica-gel; Surface

1. Introduction

Alkyl aryl ketones (**1**) containing γ-hydrogen atoms undergo characteristic 1,5-shifts through the 1,4-biradical (**2**) intermediate to yield both Norrish type II fragmentation [1] (*F*) and Yang and Yang [2] cyclization (*C*) reactions (Scheme 1). A wealth of information concerning structural and solvent effects on triplet ketone reactivities and biradical intermediate behavior has been obtained from studies in solution [3,4] the crystalline state [5] or on a solid surface [6]. Many studies have indicated that high polarity solvents with good hydrogen bonding abilities can have important effect on the relative energies of the lowest lying n,π^* and π,π^* excited states of aromatic ketones when the levels are close in energy and vibronically coupled [7,8]. In such a case, the π,π^* triplets are stabilized which is evidenced by red shifts of the π,π^* electronic transitions [9]. At the same time, the n,π^* transition is increased in energy because the lowest n,π^* state is less polar than the ground state. An electron-releasing substituent such as *p*-methyl group in the aromatic ring also stabilizes the π,π^* triplet [3,4].

Non-reactive solid supports, such as alumina or silica-gel with a high and specific porosity, may significantly control photochemical reactivity of adsorbed molecules due to electronic interactions between the molecules and the surface as well as restrictions of the conformational motion [10,11]. It is of great interest to study that not only because of an interesting chemistry but also because of an examination the nature of the surfaces themselves [12]. We wish to report here photochemistry of three alkyl aryl ketones on the surface of alumina, silica-gel and water ice as a function of surface quality and temperature: effects on the photoproduct distributions and quantum efficiencies are discussed. A possibility to perform alumina photochemistry in the microwave field has been examined.

2. Experimental part

Valerophenone and undecanophenone were purchased from Aldrich and *p*-methylvalerophenone was prepared from *p*-methylphenylmagnesium bromide and valeronitrile. Silica-gel (Merck 60), basic alumina (Merck, activity stage I; 1.1% H_2O; 0.063–0.200 mm; pH = 9.5 when stirred as 5% aqueous suspension), and acidic alumina (Aldrich, type 504C, Brockman I, 150 mesh; pH = 4.5 when stirred as 5% aqueous suspension) were used as received or dried at 400 °C for 5 h. The samples were prepared by stirring the solid support with ketone solutions in dichloromethane. The solvent was evaporated under reduced pressure and 0.5 g of the coated support was placed into Pyrex tubes and sealed under vacuum. Three-hour irradiation was stopped every

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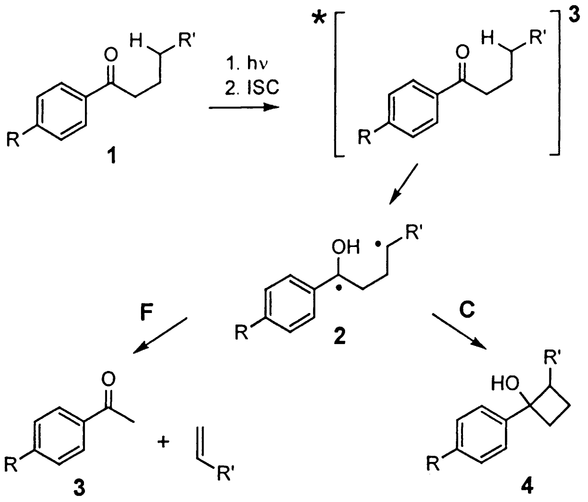


Scheme 1. The Norrish type II reaction (*F*) and Yang cyclization (*C*) of *p*-substituted alkyl aryl ketones.

15 min and the sample was shaken to refresh the surface exposed to light.

Irradiated samples were mixed with 4 ml of diethyl ether containing an internal standard and the liquid phase was analyzed by GC (a Shimadzu GC-17A apparatus and a GC/mass system TRIO 1000, FISONS Instruments). For photochemical experiments on the water ice surface, liquid water was sprayed into liquid nitrogen and the fine ice crystals were removed and mixed with pentane solution of the ketone. The organic solvent was removed in vacuo at −25 °C and the irradiation was performed in a cryostat box with ethanol as a cooling medium at the same temperature. The melted samples were extracted with dichloromethane solution of hexadecane used as an internal standard for GC measurements.

Valerophenone, *p*-methylvalerophenone, or undecanophenone adsorbed on the solid surface were irradiated by a 125 or 400 W medium-pressure mercury lamp through the 2 mm borosilicate glass filter (>280 nm experiments) or Corning CS 7-60 filter (>313 nm experiments) [13]. The only photoproducts followed for all reactants were acetophenones (**3**) and cyclobutanols (**4**). Identification of acetophenones was based on comparisons with authentic samples. Cyclobutanols were identified using GC and GC/mass instruments. Concentrations of the photoproducts were calculated from peak integrations of data obtained with flame ionization detection, assuming that the cyclobutanols had the same response as valerophenones. Formation of other photoproducts was also observed in the experiments carried out at higher temperatures. The relative quantum yield experiments were performed on a merry-go-round apparatus as described elsewhere [14].

The microwave photochemical experiments were carried out in a modified MW oven described elsewhere [31] and in a commercial reactor Synthewave 402. The oven modifications allowed irradiation from an external UV source (a 200 W high-pressure mercury lamp). We assured that most of the solution was under the direct MW radiation. In the Synthewave chamber, the vessel equipped with a condenser rotated under argon atmosphere. The MW power and temperature was controlled by Prolabo software. The vessels with the samples were connected to a very efficient water-cooled condenser by a 100–300 mm long glass tube. The microwave power was adjusted to a maximal value (800 W), which guaranteed a continual MW radiation. Circulating cool water was used in cases when a small amount (<50 ml) of a polar liquid or any amount of a non-absorbing (non-polar) liquid was used. It removed the excess of microwave power and prevented the magnetron from destruction by overheating.

3. Results and discussion

3.1. Molecular coverage of alumina surface

The molecular coverage of the solid support surface is an important information for the experimental work; only molecules in the outermost layer are responsible for the reaction. Hasegawa et al. [6] used the valerophenone (VP; **1**: R = H, R′= CH_3) photochemistry for the determination of monolayer coverage of a silica-gel surface: the coverage was found to be 100% when 5.7×10^{-4} mol of VP was loaded on 1 g of this support. Since the surface area used was 477 $m^2\,g^{-1}$ the area occupied by one molecule was 1.4×10^{-18} m^2 which corresponded well to the calculation on the basis of a space-filling model [15]. The coverage on an alumina surface in our experiments was determined according to Hasegawa's method. With an increasing VP coverage the extent of acetophenone production leveled off due to a trivial filter effect; the 100% coverage was found for $\sim 1.5 \times 10^{-4}$ mol of VP loaded on 1 g of the support, i.e. $\sim 9 \times 10^{19}$ molecules on 1 g. Since the specific surface of basic alumina used is reported to be 150 $m^2\,g^{-1}$ (Camag Standard Grade) the area occupied by one VP molecule is 1.6×10^{-18} m^2 what is in a good accord with the value obtained on silica-gel.

3.2. Fragmentation versus cyclization

There are many examples that demonstrate how various types of constraining media influence the course of photoreactions of guest molecules. The Norrish type II reaction of alkyl aryl ketones has been studied in the solid state as well as in organized media [16,17]. It is now well established that the biradical conformation, and so the elimination–cyclization ratio, is influenced by the type of the medium used, eventually preventing substantial conformational, translational, and rotational changes. Reactions are dependent on the biradical (**2**) conformation. When hydrogen abstraction occurs the triplet biradical must intersystem cross to the singlet biradical to provide singlet products. Cyclobutanol is formed when the *p*-orbitals of the radical centers can overlap. When the *p*-orbitals are parallel

Table 1
Fragmentation/cyclization ratios (*F*/*C*) of VP photochemistry[a]

Support/solvent	Temperature (°C)	*F*/*C*
Silica-gel (dry[b])	−20	6.0 ± 0.2
Silica-gel (dry)	0	6.0 ± 0.3
Silica-gel (dry)	20	5.8 ± 0.2
Silica-gel (wet[c])	20	5.0 ± 0.2
Basic alumina (dry[b])	−20	9.9 ± 0.3
Basic alumina (dry)	0	9.1 ± 0.4
Basic alumina[d] (dry)	20	10.5 ± 0.5
Basic alumina (wet[c])	20	11.2 ± 0.4
Water ice surface	−25	6.0 ± 0.3
Water ice (inclusion)	−30	3.6[e]
Liquid water	20	1.9[f]
Liquid acetonitrile	20	5.7[g]
Liquid hexane	20	6.7[g]

[a] Irradiated at >280 nm; mean ± standard deviation for five separate experiments. The amount of ketone used was 6×10^{-5} mol g^{-1}.
[b] The solid support was heated at 400 °C for 5 h.
[c] The 2% (w/w) of water.
[d] The *F*/*C* ratio in acidic alumina was slightly higher.
[e] From [20].
[f] From [18].
[g] From [19].

to the C_β–C_γ bond, this bond will cleave to give an enol and an alkene [3,4].

In this work, type II cleavage to acetophenone and alkene always dominated over the Yang cyclization to 1-phenyl-2-alkylcyclobutan-1-ols in the photolysis of VP and undecanophenone (UP; **1**: R = H, R′ = $(CH_2)_6CH_3$) on surfaces of silica-gel, alumina, and water ice. The ketone coverage of the first two supports was chosen to be <50% in order to guarantee that all molecules are in the contact layer with the support. The results show that the *F*/*C* ratios were generally higher on alumina (∼10) than those on silica-gel (∼6) for both VP (Table 1) and UP (Table 2). The ratios did not change with temperature in the region of −20 to 20 °C. Cleavage is considerably more efficient to occur on a support, especially on alumina, than that observed in polar liquid water [18] or acetonitrile [19]. Water ice surface provided a similar regioselectivity as that of silica-gel. The fact that the length of alkyl chain as well as temperature had insignificant effects on the ratio means that the conformational freedom of ketones on the surface is large. The differences in the *F*/*C* values found on silica-gel and alumina suggest the existence of a specific interaction between the molecules and the surface. To determine the character of interactions we carried out a series of the relative quantum yield measurements.

Table 2
Fragmentation/cyclization ratios (*F*/*C*) of UP photochemistry[a]

Support/solvent	Temperature (°C)	*F*/*C*
Silica-gel (dry[b])	−20	5.5 ± 0.3
Silica-gel (dry)	0	6.7 ± 0.5
Silica-gel (dry)	20	5.1 ± 0.2
Silica-gel (wet[c])	20	5.0 ± 0.2
Basic alumina (dry[b])	−20	10.1 ± 2.3
Basic alumina (dry)	0	14.8 ± 0.8
Basic alumina (dry)	20	10.6 ± 0.9
Basic alumina (wet[a])	20	10.6 ± 0.4
Water ice surface	−25	>10[d]

[a] Irradiated at >280 nm; mean ± standard deviation for five separate experiments. The amount of ketone used was 6×10^{-5} mol g^{-1}.
[b] The solid support was heated at 400 °C for 5 h.
[c] The 2% (w/w) of water.
[d] The reproducibility was low.

Table 3
The quantum efficiency ratios for VP and MeVP photolysis at >313 nm

Support/solvent	Coverage/concentration of ketones	***R***[a]
Basic alumina	∼6×10^{-5} mol g^{-1}	4.3
Acidic alumina	∼6×10^{-5} mol g^{-1}	2.3
Silica-gel	∼6×10^{-5} mol g^{-1}	2.0[b]
Water ice[c]	∼10^{-5} mol g^{-1}	7.4
Cyclohexane	0.01 M	1.2
Methanol	0.01 M	1.7 (2.0)[b]
0.5 M pyridine[d]	0.01 M	1.3 (1.0)[b]
Liquid water	∼10^{-5} M	0.7 (1.1)[e]

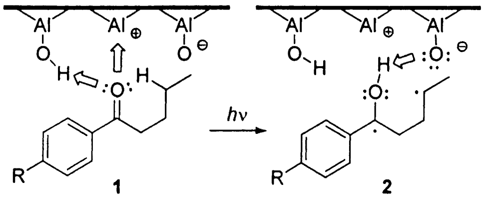
Cyclohexane solution of pyridine.
[a] $\boldsymbol{R} = ([\mathbf{3}] + [\mathbf{4}])_{VP}/([\mathbf{3}] + [\mathbf{4}])_{MeVP}$. The reproducibility in all experiments was ±8%.
[b] The quantum yield ratios from [6].
[c] Irradiated mixture of VP and MeVP at >280 nm.
[d] In cyclohexane.
[e] The quantum yield ratio.

3.3. Quantum yield measurements on alumina and water ice

Table 3 displays the data from irradiation of the VP and *p*-methylvalerophenone (MeVP; **1**: R = CH_3, R′ = CH_3) samples. The ratio of photoproduct concentrations, defined as $\boldsymbol{R} = [([\mathbf{3}]+[\mathbf{4}])_{VP}/([\mathbf{3}]+[\mathbf{4}])_{MeVP}]$, is the ratio of photochemical reaction efficiencies. The efficiencies are not corrected on molar absorption coefficients. Alumina absorbs UV radiation in the region of interest but it still is partially transparent to allow photochemistry in the whole volume of our samples. The molar absorption coefficients at 313 nm are smaller by about 30% for VP than those for MeVP in ethanol or cyclohexane [21]. Provided that their values are similar on the solid supports the actual ratios ***R*** would be slightly smaller than those of the corresponding quantum yields. ***R*** was found considerably higher on a basic alumina than that on an acidic alumina by a factor of 2 due to the fact that while the relative quantum yields of VP type II reaction *changed* those of MeVP remained same. The ***R*** value from the water ice experiments, obtained from irradiation of a mixture of VP and MeVP, is not corrected on the bimolecular triplet energy transfer between the ketones [6]. Moreover, there is a high possibility that the coverage was higher than 100% (the surface of ice crystals must be significantly smaller that that of alumina or silica-gel). Since the quantum yields of the VP and MeVP photolyses in liquid water were found to be almost unity, the ***R*** value of 7.4 is definitively intriguing.

Surface of amphoteric alumina is extremely complicated. Knözinger and Ratnasamy proposed five possible coordinations of the OH group attached either to one, two or three Al atoms [21]. Such groups bear slightly differing net charges; as a consequence, they posses different protonic acidity [22]. In addition to hydroxyl groups on the alumina surface (their number depends on the extent of dehydration), acidic (Al^+) and basic (O^-) sites can also alter a surface chemistry [23,24]. Basicity of alumina is suppressed by addition of HCl (acidic alumina). It is well known that the kinetics and the product distribution of the Norrish type II reaction of alkyl aryl ketones is significantly controlled by solvent properties: (a) high dielectric and polar solvents affect the relative energies of the lowest lying n,π^* and π,π^* excited states, and (b) hydrogen bonding solvents interact with 1,4-hydroxy biradical intermediates causing slowing down the disproportionation of the biradical intermediate to starting ketone [3,4]. Since both acidic and basic sites are present on amphoteric alumina surface one can propose a model in which (1) acidic sites coordinate to the carbonyl oxygen (the Brönsted OH groups and Lewis aluminum ions provide a strong polar environment for the carbonyl group of the ground or excited state ketone **1**), and (2) the basic O^- group is involved in hydrogen bonding with the OH group of the biradical intermediate (Scheme 2).

The enhanced quantum yields of VP photochemistry, reaching nearly unity in polar ethanol or acetonitrile, are a consequence of solvation of the biradical intermediate rather than of any interaction with the excited molecule [19,25,26]. However, Hasegawa et al. reported the relative quantum yield ratios for acetophenone formation (Φ_{AP}/Φ_{MeAP}) equal to 1 in a solution of added Lewis base (pyridine) but $\Phi_{AP}/\Phi_{MeAP} = 2$ in methanol and silica-gel surface. The authors reasoned that it is caused by the inversion of the lowest π,π^* and n,π^* triplet states in MeVP [6]. We have recently studied the quantum efficiency ratios ***R*** in various solvents as a function of temperature. The quantum efficiency differences were reported to be caused by both the carbonyl group and biradical OH group solvation [27]. It was shown that such a small structure change as the *para*-methyl substitution in MeVP altered the temperature dependent photoreactivity in presence of weak bases. The experimental results suggested that the hydrogen bonding between the biradical intermediate OH group and the solvent is weaker for MeVP than that for VP at 20 °C and that the interactions vanish in both ketones at 80 °C. In this work, *only* the increase in the relative quantum yield of VP photolysis is responsible for the fact that ***R*** doubled on basic alumina comparing to acidic alumina (Table 3). Furthermore, when the reaction was carried out at a higher temperature (40–60 °C) the ratio dropped, possibly because the interactions weakened. A high value of ***R*** on basic alumina must be connected to the increasing number of basic (O^-) sites on the surface. If the interactions between the carbonyl group and an acidic site were responsible for changing the ***R*** values the effect should be opposite. The biradical OH group is the only acidic site in the course of the reaction capable of hydrogen bonding formation, thus the selectivity must occur as a consequence of the methyl substitution in MeVP that lowers the biradical OH group acidity comparing to that of unsubstituted VP. The biradical lifetimes of alkyl aryl ketones are in order of 10–100 ns, depending on the solvent used, [28] which may be long enough for adjusting the molecule into a favorable conformation allowing an interaction with the surface.



Scheme 2. Surface interactions on alumina.

In summary, we propose that the short-lived biradical intermediate interacts with the surface of alumina (and correspondingly with other surfaces) in addition to polar effect on the excited triplet of ketone.

3.4. Microwave photochemical experiments on alumina

Photochemistry of alkyl aryl ketones adsorbed on alumina was investigated in the microwave field as a part of our program on microwave photochemistry, [29–33] in which a simultaneous effect of both ultraviolet and microwave (MW) irradiation on chemical reactivity is studied. MW activation increases efficiencies of many chemical processes at the same time as it can reduce formation of by-products, otherwise obtained from conventionally heated reactions. Utilization of alumina for MW chemistry is currently a dynamically developing issue [34–36]. Based on the results from preliminary experiments [37] we have attempted to study the Norrish type II reaction of VP and MeVP on alumina under MW photochemistry conditions. The MW field causes a rapid heating of the support but the support temperature can be controlled without difficulties. Same photoproduct distribution was obtained from experiments, in which temperature was kept below 40 °C, however, raising the temperature caused a production of some amount of unidentified photoproducts (while no "dark" photochemistry was observed), some of them of a higher molecular weight. Irradiation of a mixture of VP and MeVP on basic alumina produced a gradual drop of the ***R*** values with increasing temperature: the value decreased by a factor of 2 when going from 20 to 60 °C. This well corresponds to our proposal according to which the biradical OH group interacts with basic sites on the surface and the interactions weaken with increasing temperature. The advantage of using the MW irradiation for alumina photochemistry is especially in simplicity of both the experiment arrangement and the reaction temperature control. The MW photochemistry of other photochemical systems adsorbed on a solid support is currently under investigation.

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