

## TEMPERATURE EFFECTS ON THE PHOTOISOMERIZATION KINETICS AND MECHANISM OF CARVONE AND ACETOXYISOPIPERITENONE <sup>1</sup>

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**ABSTRACT.** Temperature effects on the photoisomerization kinetics of carvone (CAV) and acetoxyisopiperitenone (AIP) were investigated. First order rate constants were determined in the temperature range of 273 K - 307 K. Thermodynamic activation parameters ( $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$ ) were measured for CAV and AIP photoisomerization in acetonitrile and ethanol.  $\Delta G^*$  and  $\Delta H^*$  values were found to be significantly smaller for AIP than for CAV. This indicates a lower activation energy barrier in the case of AIP than that of CAV. The strongly negative values of  $\Delta S^*$  are discussed in terms of photoisomerization mechanism.

### INTRODUCTION

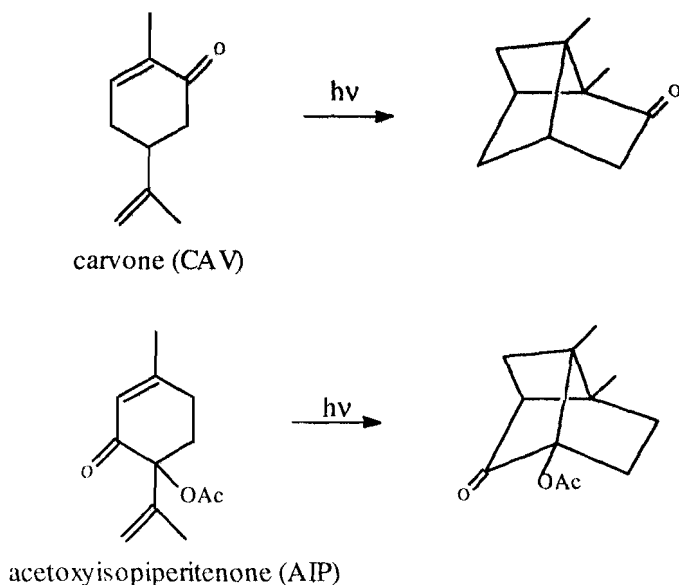
The interest in using valence photoisomerization reactions of norbornadiene derivatives for light energy photochemical conversion and storage systems has been shown recently by several authors [1-5]. Carvone photoreactions such as photoisomerization have also been studied, especially because of possible applications to light energy photochemical storage [6-11]. Recently, we have evaluated the photoisomerization of carvone and acetoxyisopiperitenone for similar purposes [12-14].

As a continuation of our studies, we have investigated in this work, the temperature effects on the photoisomerization of carvone (CAV) and acetoxyisopiperitenone (AIP) (Scheme I) in acetonitrile and ethanol aimed at optimizing the experimental conditions for solar energy storage systems and to obtain information on the photoisomerization mechanisms of AIP and CAV. Activation thermodynamic parameters ( $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$ ) as well as storage enthalpies were determined for the photoisomerization of these compounds.

### EXPERIMENTAL

*Chemicals.* Carvone (CAV) was purchased from Aldrich. Acetoxyisopiperitenone (AIP) was synthesised according to the procedure of Erman and Gibson [15] by treating 0.1 mol of piperitenone with 0.4 mol of lead tetraacetate. The solvents used were spectroscopic grade acetonitrile and ethanol (Aldrich).

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Scheme 1

*Methods.* Solutions of CAV or AIP were irradiated at different temperatures in a 1-cm quartz cuvette using an Ostram HBO 200 W high pressure mercury lamp placed in an Oriel model 6137 housing or by direct irradiation from sunlight. To filter the output of the lamp, an interferential glass filter was located on the optical path giving a  $340 \pm 10$  nm light. Photochemical experiments were carried out after bubbling nitrogen through the solution. All solutions used were stirred magnetically during irradiation.

## RESULTS AND DISCUSSION

*Temperature effects.* In our previous papers [12-14], the photoproduct distribution, kinetics, and quantum yield of AIP and CAV direct photoisomerization were investigated in several solvents of various polarities.

The study of the temperature effect on the rate constants of CAV and AIP, photoisomerization was monitored spectrophotometrically by measuring the decrease in the absorption peak with irradiation time at temperatures ranging between 273 and 307 K, for a CAV (or AIP) concentration of  $3 \times 10^{-5}$  M. Overall first-order rate constants were obtained at all temperatures under study, i.e. the plots of  $\log(A_{t=0}/A_t)$  against the illumination time,  $t$ , were linear. The overall first order rate constant ( $k_1$ ) increased significantly with increasing temperatures (Figure 1). The increments in  $k_1$  were about 30% from 273 K to 307 K. The values of  $k_1$  are significantly larger for AIP than for CAV.

*Thermodynamic activation parameters.* Thermodynamic activation parameters of CAV and AIP photoisomerization were determined by means of the Wynn-Jones-Eyring equation:

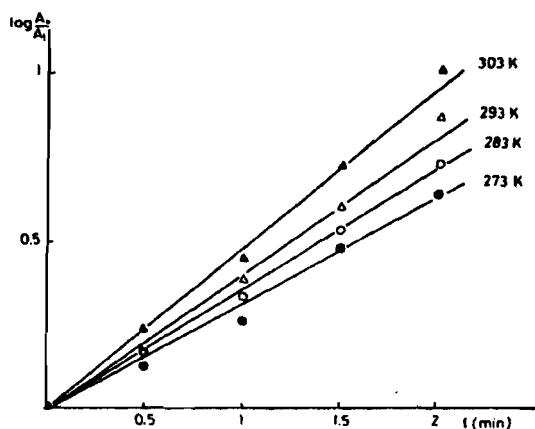


Figure 1. Temperature effect on the photoisomerization rate of AIP ( $3 \times 10^{-5}$  M) in ethanol.

$$k_1 = k_B \cdot T/h \cdot e^{-\Delta G^*/RT} = k_B \cdot T/h \cdot e^{(\Delta S^*/R - \Delta H^*/RT)} \quad (1)$$

where  $k_B$  = Boltzman's constant;  $h$  = Planck's constant;  $\Delta G^*$ ,  $\Delta H^*$  and  $\Delta S^*$  are the activation free energy, the activation enthalpy and the activation entropy, respectively.

The value of  $\Delta H^*$  and  $\Delta S^*$  were obtained by plotting  $(\ln k_1 - \ln T)$  against  $1/T$ , according to equation 2:

$$\ln k_1 - \ln T = \ln(k_B/h) + \Delta S^*/R - \Delta H^*/RT \quad (2)$$

The results are presented in Table 1 and Figure 2. The  $\Delta G^*$  values are relatively close to those reported for the photocyclization of diphenylamines [16]. The data in Table 1 also reveal that the  $\Delta G^*$  and  $\Delta H^*$  of photoisomerization of AIP are significantly smaller than those of CAV, which implies a lower activation energy barrier for AIP. Moreover, the strongly negative  $\Delta S^*$  values for both compounds (-260 and -277 J/mol K) show that the molecular configurations of the transition states of carvone and AIP are more ordered than in the initial states.

Table 1. Thermodynamic activation parameters at 303 K for the photoisomerization of carvone and acetoxyisopiperitenone.

Thermodynamic activation parameters	Carvone		Acetoxyisopiperitenone	
	EtOH	MeCN	EtOH	MeCN
$\Delta G^*$ (kJ/mol)	97.2	99.0	86.8	87.8
$\Delta H^*$ (kJ/mol)	14.2	15.1	8.05	8.79
$\Delta S^*$ (J/mol/K)	-274	-277	-260	-261

*Mechanisms of CAV and AIP photoisomerization.* The photoisomerization mechanism of carvone has given rise to several controversies [7, 8]. Indeed, Buchi *et al.* [6] have proposed a diradical mechanism, while Meinweld and Scheinder [7] have suggested a zwitterion mechanism. Taking into account our  $\Delta S^*$  negative values, which indicate a diminution of degrees

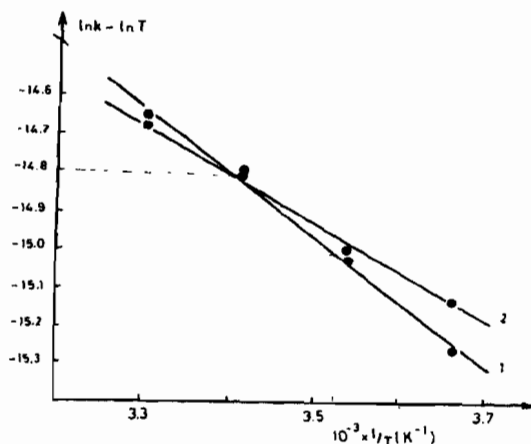
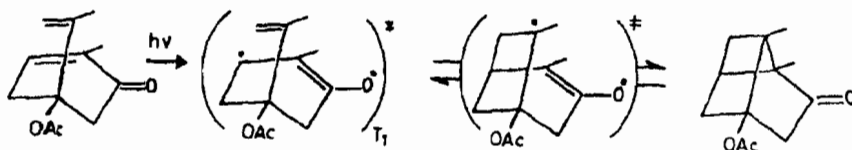
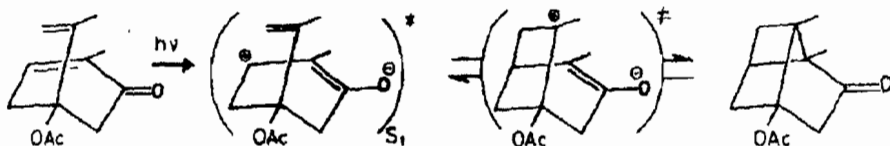


Figure 2. Wynn-Joes-Eyring curves (1) carvone and (2) acetoxyisopiperitenone in acetonitrile of freedom in the transition state, relative to the initial state, two mechanisms can be postulated (Schemes II and III):



Scheme II



Scheme III

The first mechanism is a diradical mechanism (Scheme II) in which the  $n - \pi^*$  excited state of the carbonyl group ( $C=O$ ) would play an important role as an internal photosensitizer. In this case, a triplet charge transfer would occur probably between the  $C=O$   $n, \pi^*$  excited state and the endocyclic orbital.

The second mechanism is the zwitterion mechanism, which implies the intervention of a radical-cation in the transition state (Scheme III).

However, the  $\Delta S^*$  values are only slightly different in the two studied solvents (MeCN and EtOH), suggesting a similar solvation of the transition state in both solvents. This result is in agreement with a diradical mechanism.

*Application to light energy photochemical storage.* From the two systems under study, we decided to test the AIP system for its possible use in the photochemical storage of light energy. Indeed, the photoisomerization rate constants and quantum yields are significantly higher for AIP than for CAV. Moreover, the photoreactions are cleaner in aprotic solvents. Therefore, we studied spectrophotometrically the sunlight irradiation of AIP in different solvents by monitoring the decrease in the peak absorbance at 237 nm with sunlight irradiation time. This decrease, which occurred in all the solvents under study, is due to the formation of the non-conjugated, weakly UV absorbing photoproduct dimethyltricyclo-[3,3,O]-octan-6-one (ADTO), as shown previously [14].

The photoreactions obeyed first-order kinetics since plots of  $\log(A_{t=0}/A_t)$  vs sunlight irradiation time were linear in all solvents (Figure 3), similar to irradiation with high-pressure mercury lamp. The observed rate constants are shown in Table 2.

We calculated the photoisomerization storage enthalpies from bond energies, and we found a value of 126 kJ/mol for AIP. This value is significantly larger than the reported value (104 kJ/mol) for norbornadiene [17].

Table 2. Rate constants of the photoisomerization of acetoxyisopiperitenone under sunlight irradiation in various solvents<sup>a</sup>.

Solvent	k (min <sup>-1</sup> )	Correlation coefficient	Temperature (K)
Acetonitrile	0.22	0.999	304
Ethanol	0.24	0.999	304
Dioxane	0.24	0.999	307
Cyclohexane	0.22	0.999	307

<sup>a</sup>Conditions of solar irradiation: on the top of Paris 7 University, on a sunny day (August 1993).

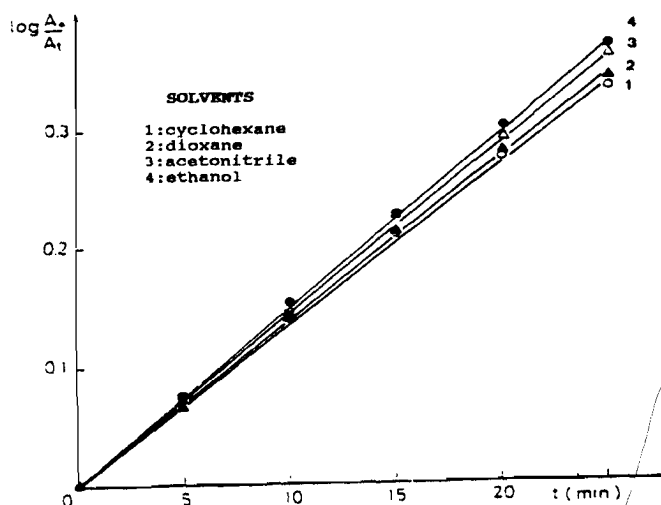


Figure 3. Photoisomerization kinetic plots for AIP in various solvents under solar irradiation.

## CONCLUSION

The photoisomerizations of CAV and AIP fulfil several requirements of a light energy photochemical storage system [18, 19]. Because of its lower activation free energy value, the photoisomerization of AIP can be considered more convenient than that of carvone for photochemical storage. The strongly negative values of  $S^*$  support the diradical mechanisms for CAV and AIP photoisomerization. Finally, AIP photoisomerization is also a suitable system for storage of light energy, since it reflects a relatively large storage enthalpy value.

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