

Polymerizable Tautomers II.[†] Solvent Effect on Tautomerism and Polymerization of Ethyl 4-Methyl-3-oxo-4-pentenoate

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ABSTRACT: This paper describes solvent effect on tautomerism and polymerization of ethyl 4-methyl-3-oxo-4-pentenoate, which is in coexistence with two tautomers. The ketonic form is predominant in polar solvents and the enolic one in non-polar solvents. The tautomeric equilibria depend on polarity and hydrogen-bond donating power of the solvents. The homopolymerization and the copolymerization with styrene in polar and non-polar solvents reveal that there are a negligible interaction between EMAA monomer and the solvent, and a specific solvation of the polymer radical having EMAA unit as the terminal group. The enolic-type radical is more reactive than the ketonic one.

KEY WORDS Ethyl 4-Methyl-3-oxo-4-pentenoate / Polymerizable
Tautomer / ¹H and ¹³C NMR / Equilibrium Constant / Solvent Effect /
Radical Polymerization and Copolymerization /

Since the work of Nazarov and Zavyalov² the usefulness of esters of 3-oxo-4-pentenoic acid for a Robinson annelation³ and a Mannich reaction for the construction of the piperidine ring⁴ has been demonstrated. However, the esters have never been chosen as the subject of the study of polymerization.

Our great interest is focussed on vinyl compounds with a tautomeric substituent, particularly with a keto-ester group. Ethyl 4-methyl-3-oxo-4-pentenoate (ethyl methacryloyl acetate, abbreviated EMAA) is in coexistence with two tautomers, *i.e.*, the ketonic and enolic forms. Therefore, homopolymerization of EMAA can be regarded as copolymerization of the keto- and enol-type monomers, and the keto-enol equilibria seem to

be one of factors governing rate of polymerization and copolymerization parameters.

In the present paper, we discuss the solvent effect on tautomerism of EMAA, using multiparametric regression analysis and empirical polarity parameters, according to the "Linear Solvation Energy Relationship".⁵ Additional investigation has been done for obtaining preliminary data on polymerizability of the tautomers of EMAA.

EXPERIMENTAL

EMAA was prepared according to the procedure of Stork.⁶ bp 70—72°C [5 mmHg (0.67 kPa)]. The solvents were commercially available and purified by the standard meth-

[†] Part I of this series is ref 1.

ods prior to use. Polymerization and copolymerization in benzene and dimethyl sulfoxide (DMSO) were carried out at 60°C in sealed tubes with 2,2'-azobisisobutyronitrile (AIBN) as the initiator. After a given time, the contents were poured into a large excess of methanol or petroleum ether, and the resulting polymers were filtered off, dried under reduced pressure, and then weighed. The polymerization rate and the copolymer composition were determined by gravimetric and elemental analyses, respectively.

For the determination of the equilibrium

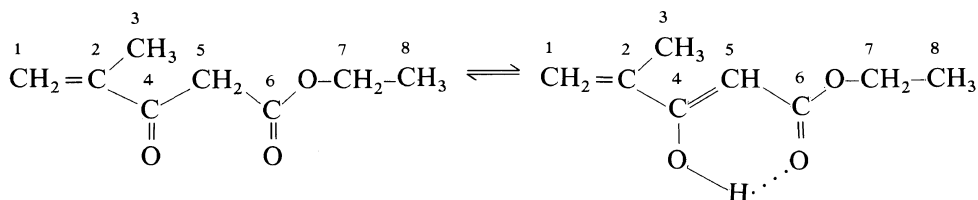


Table I shows NMR chemical shifts of EMAA. The spectral data reveal that EMAA is in coexistence with two tautomers, *i.e.*, the ketonic and enolic forms. The keto-enol interconversion is sufficiently slow on NMR time scale that the tautomeric constant can be calculated from area obtained by integration of the singlet peaks at 3.73 and 5.23 ppm

Table I. ^1H and ^{13}C NMR chemical shifts of EMAA^a

Proton	Chemical shift		Carbon	Chemical shift	
	ppm			ppm	
	Keto	Enol		Keto	Enol
C ₁ -H	6.87	5.34	C-1	126.5	120.1
	6.00	5.89	C-2	144.6	137.7
C ₃ -H	1.83	1.88	C-3	17.3	18.3
C ₅ -H	3.73	5.23	C-4	167.8	171.4
C ₇ -H	4.12	4.19	C-5	45.2	88.8
C ₈ -H	1.21	1.26	C-6	194.2	173.5
O-H	12.16		C-7	61.1	60.7
			C-8	14.3	14.4

^a Measurement were carried out without solvent at 24°C.

constant, the ^1H NMR spectra of EMAA were measured in hydrogenated solvents at 24°C on a JEOL GX-400 spectrometer, the concentration being 0.077 mol dm⁻³.

RESULTS AND DISCUSSION

Tautomerism of EMAA

Generally, keto-ester compounds are possible to have tautomeric structures. For example, tautomerization of EMAA is expressed as follows:

which are assigned to the methylene and methyne protons lying between two carbonyl groups, respectively. As can be seen from Table II, the ketonic fraction in EMAA increases with an increasing polarity of solvents. Such a tendency is widely noted in

Table II. Equilibrium constant (K_T) for the tautomerization of EMAA^a

No.	Solvent	Ketonic fraction	K_T
1	Hexane	0.370	0.588
2	Triethylamine	0.374	0.596
3	Carbon tetrachloride	0.389	0.637
4	Benzene	0.492	0.968
5	1,2-Dimethoxyethane	0.733	2.743
6	Ethyl acetate	0.748	2.971
7	Acetonitrile	0.796	3.900
8	Acetone	0.798	3.943
9	Pyridine	0.822	4.615
10	Dimethylformamide	0.856	5.944
11	Methanol	0.860	6.153
12	Dimethyl sulfoxide	0.891	8.149

^a Measurement were carried out at 24°C in hydrogenated solvents with the concentration of 0.077 mol dm⁻³.

tautomerism of keto-ester compounds such as ethyl acetoacetate.

As quantitative description of the solvent effects on chemical processes and spectroscopic properties, linear multiparametric equations have been proposed by many authors.⁷⁻¹¹ Taft *et al.* have also proposed a "Linear Solvation Energy Relationship" as the empirical solvent scale,⁵

$$x = x_0 + s(\pi^* + d\delta) + a\alpha + b\beta$$

where π^* (polarity), δ (polarizability), α (hydrogen-bond donating power), and β (hydrogen-bond accepting power) are referred to as the solvatochromic parameters, and s , d , a , and b as the solvatochromic coefficients, respectively. This equation is regarded as a general representation of the solvent effect because of a better correlation between solvatochromic parameters and other empirical solvent scales.¹²

Figure 1 shows regression analysis of the equilibrium constant with the solvatochromic parameters. The application of the Kamlet-Taft equation⁵ to our tautomeric system gives a good linear correlation

$$\ln K_T = -0.648 + 2.811(\pi^* - 0.262\delta) + 0.737\alpha + 0.059\beta \quad R = 0.967$$

A comparison of the solvatochromic coefficients shows that the tautomeric equilibria are dependent on the polarity and hydrogen-bond donor acidity of the solvents. In EMAA-solvent interaction, the solvents may serve as hydrogen-bond donor for the ketonic tautomer and as hydrogen-bond acceptor for the enolic one. Therefore, much contribution of the solvent acidity is presumed to result from preponderance of the ketonic form of EMAA.

The equilibrium constant of EMAA changes also with concentration of solute and temperature. The NMR measurements of EMAA were carried out in two typical solvents, acetonitrile of a polar solvent and

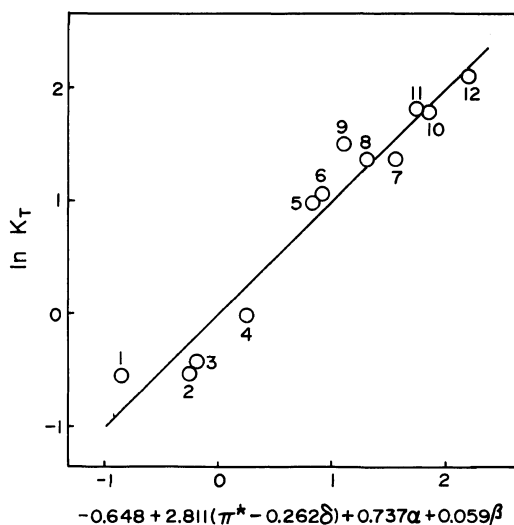


Figure 1. Regression analysis of equilibrium constants with the solvatochromic parameters. Same symbols as in Table II.

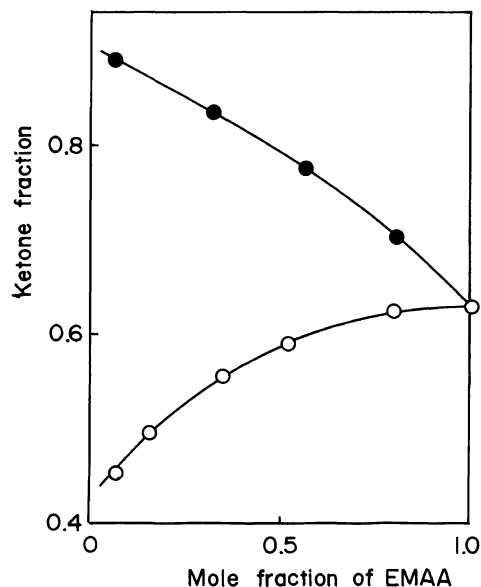


Figure 2. Influence of dilution on the ketonic fraction of EMAA in carbon tetrachloride (O) and acetonitrile (●).

carbon tetrachloride of a non-polar solvent. As can be seen from Figure 2, the tautomeric equilibria exhibit a remarkable dependence on the EMAA concentration. Therefore,

the equilibrium constants obtained are the observed. Dilution with carbon tetrachloride favors shift of the equilibrium to the enolic tautomer, whereas opposite effect should occur in acetonitrile solution. These concentration effects probably result from differences between polarities of solvent and solute and/or solute-solvent interactions. Since the measurements were carried out in such higher concentration as the solution is not considered to be the ideal solution and as polymerization of EMAA are actually performed, the appearance of the concentration effect may be inevitable. Similar concentration effect on tautomeric equilibria has been reported by Roussel *et al.*¹³

Figure 3 shows the temperature dependence of the equilibrium constant. The equilibrium of EMAA in carbon tetrachloride shifts toward the ketonic tautomer with an increase in temperature, whereas the use of acetonitrile as the solvent takes the opposite effect. Enthalpy and entropy differences between the ketonic and enolic tautomers were found to be $\Delta H = -2.07 \text{ kcal mol}^{-1}$ and $\Delta S = -6.18 \text{ cal mol}^{-1} \text{ K}^{-1}$ for carbon tetra-

chloride solution, and $\Delta H = 1.10 \text{ kcal mol}^{-1}$ and $\Delta S = 8.07 \text{ cal mol}^{-1} \text{ K}^{-1}$ for acetonitrile solution, respectively.

Polymerization of EMAA

The polymerization was carried out at 60°C with $[\text{EMAA}] = 1.46 \text{ mol dm}^{-3}$ by use of polar and non-polar solvents. As can be seen from Figure 4, the rate of polymerization in benzene is higher than that in DMSO. The ketonic fraction in EMAA is 0.492 in benzene and 0.891 in DMSO, at the concentration of $0.077 \text{ mol dm}^{-3}$. The equilibrium constant depends on the concentration of the solute (EMAA), temperature, and solvents. Though the fraction of each tautomer under conditions that the polymerization was performed is not determined, it is obvious that the enolic fraction is predominant in the non-polar solvent and the ketonic one in the polar solvent.

The copolymerization of EMAA (M_1) and styrene (M_2) was carried out using the same solvents as in the case of homopolymerization. The copolymerization parameters ob-

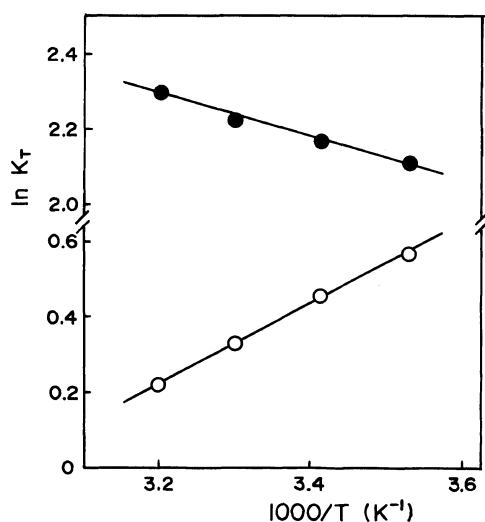


Figure 3. Temperature dependence of equilibrium constants for tautomerization of EMAA in carbon tetrachloride (○) and acetonitrile (●).

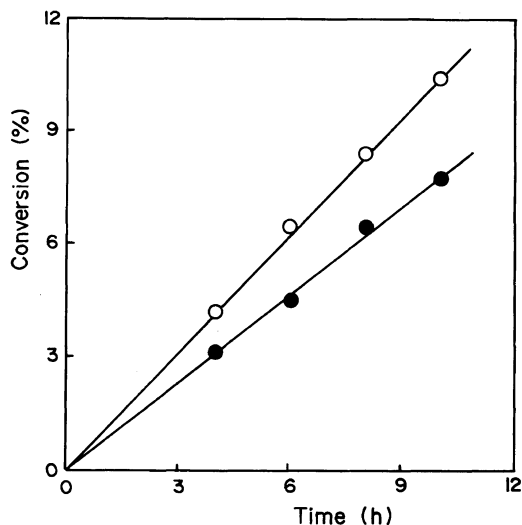


Figure 4. Time-course of conversion for the polymerization of EMAA at 60°C in benzene (○) and DMSO (●). $[\text{EMAA}] = 1.46 \text{ mol dm}^{-3}$, $[\text{AIBN}] = 2 \times 10^{-2} \text{ mol dm}^{-3}$.

Table III. Copolymerization parameters for the EMAA (M_1)-styrene (M_2) system

Solvent	r_1	r_2	Q_1	e_1
Benzene	0.67	0.13	2.20	0.76
DMSO	0.46	0.10	2.43	0.95

tained are listed in Table III. r_1 - and r_2 -values are dependent on and independent of the solvents, respectively. Monomer reactivity ratio r_2 is the ratio of the rate constants for addition of two monomers toward the polymer radical with styrene unit at its terminal position. No difference in r_2 -value suggests a negligible interaction between EMAA monomer and the solvent. On the other hand, there is a significant effect of the solvent on r_1 . Monomer reactivity ratio r_1 represents the ratio of rate constants for addition of EMAA and styrene toward the polymer radical with EMAA unit as the terminal group. Since the reactivity of styrene is supposed to be independent of the solvent, negligible interaction between EMAA and the solvent, as described above, suggests a specific solvation of the propagating polymer radical having EMAA as the terminal unit.

The polymerization rate depends on the reactivities of both polymer radical and monomer, and much contribution of the former is generally considered. The enolic form of EMAA monomer, of course, predominant in a non-polar solvent, and the ketonic form in a polar solvent. However, the keto/enol ratio of EMAA unit in the polymer is not always equal to that of the monomer. The enolic fraction in the polymer was measured on a ^1H NMR spectrometer and found to be 0.33 and 0.30 in benzene- d_6 and DMSO- d_6 , respectively. This finding shows that the enolic fraction in the polymer is approximately equal in both solvents. The corresponding equilibrium may be true for the terminal EMAA radical along the polymer chain. Even if so, however, it seems reason-

able to assume that DMSO has more solvent effect on the propagating polymer radical than benzene does.

CONCLUSIONS

EMAA is an equilibrium mixture of two tautomers, the ketonic and enolic forms. The former is predominant in a polar solvent and the latter in a non-polar solvent. Regression analysis of the equilibrium constant with the solvatochromic parameters revealed that the tautomeric equilibria depend on polarity and hydrogen-bond donor acidity of the solvents. However, the keto/enol ratio of EMAA unit in the polymer is independent of the solvent used.

The polymerization of EMAA is faster in a non-polar solvent than in a polar solvent. The results of the copolymerization of EMAA and styrene suggest that there are a negligible interaction between EMAA monomer and the solvent, and a specific solvation of polymer radical having EMAA unit at its terminal position.

REFERENCES

1. S. Masuda, M. Tanaka, and T. Ota, *Makromol. Chem.*, **187**, 1087 (1986).
2. N. Nazarov and S. I. Zavyalov, *Zh. Obshch. Khim.*, **23**, 1793 (1953).
3. E. Wenken, A. Afonso, J. B. son Brendenberg, C. Kaneko, and A. Tahara, *J. Am. Chem. Soc.*, **86**, 2038 (1964).
4. K. Hohenlohe-Oeringen, *Monatsh. Chem.*, **93**, 578 (1962).
5. M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 337 (1979).
6. G. Stork and Nath Guthikonda, *Tetrahedron Lett.*, 2755 (1972).
7. K. Dimroth, C. Reichadt, T. Seipmann, and F. Bohlman, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).
8. A. Allerhand and P. V. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 374 (1963).
9. L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkins, and L. L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2433 (1965).
10. S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).
11. B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.*, **98**, 4395 (1976).

12. J. L. Abboud, M. J. Kamlet, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 8325 (1977). 13. R. Roussel, M. Oteyza de Guerrero, P. Spegt, and J. C. Galin, *J. Heterocyclic Chem.*, **19**, 785 (1982).