both fail to account for the large observed α-protonation shifts. On the other hand bond-order terms, arising from important two-center integrals, are required to transfer to the α carbon the effect of the changes in the effective ΔE arising primarily in protonation from a change in the n–π^* or NH–π^* energy separation. It is now felt that a combination of both features is required to explain best anomalous shifts in α carbons at the present time.

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An Electron Spin Resonance Study of the Kinetics of Recombination of Tri-*t*-butylcycloheptatrienyl Radicals[1]

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Abstract: Few measurements of recombination rate constants for hydrocarbon free radicals in liquid solution have been reported. The goal of this work is to measure the rate of recombination of the tri-*t*-butylcycloheptatrienyl radical using a simple esr technique. This free radical is generated by photochemical cleavage of hexa-*t*-butylbicycloheptatrienyl in *n*-pentane. The recombination rate has been measured $(-112^\circ \leqslant t \leqslant +22^\circ)$ by terminating the illumination and monitoring the second-order decay of the esr signal on a strip-chart recorder. Absolute rate constants are obtained by comparison of the steady-state esr intensity with that of a solution of di-*t*-butylnitroxide of known concentration. Typical approximate rate constants are $3 \times 10^4 M^{-1}$ sec^{-1} at -105° and $3 \times 10^5 M^{-1}$ sec^{-1} at $+22^\circ$ and the Arrhenius activation energy is 1.7 ± 0.3 kcal/mol. The rate of recombination is compared with that of other hydrocarbon free radicals in solution.

Although the rates of free-radical reactions in liquid solution are of great interest,[3] few measurements of recombination rates have been reported for small, *i.e.*, monomeric, hydrocarbon radicals.[4] Of these only the study of ethyl radical has employed esr spectroscopy.[5]

We have therefore investigated the recombination kinetics of tri-*t*-butylcycloheptatrienyl radical. The esr spectrum of this radical has been discussed elsewhere.[6] This choice of a system (1) leads to the utilization of a much simpler esr technique than that required for the alkyl radicals[4,5] since the recombination rate constant is considerably smaller and (2) reflects our continuing interest in the esr of π-electron free radicals containing seven-membered rings.[6,7]

Experimental Section

Most of the experimental details have been described elsewhere.[6] These include the synthesis of hexa-*t*-butylbicycloheptatrienyl, sample-preparation technique, materials used as solvents, esr spectrometer employed, and the apparatus to vary the sample temperature.

Rate constants for radical recombination were measured as follows. Deoxygenated samples of hexa-*t*-butylbicycloheptatrienyl in *n*-pentane were placed in a Varian Associates dual cavity and were illuminated *in situ* using the full output of a Hanovia 140W high-pressure mercury lamp (Model SH). The esr spectrum of the tri-*t*-butylcycloheptatrienyl radical was detected. Sample illumination was terminated by means of a shutter. The decay of the peak height of the central component of the esr spectrum was monitored using a Honeywell Electronik 19 strip-chart recorder.[8] Recombination rate constants, k_{-1}, were obtained from the slopes of the plots of C_0/C *vs.* time, which were linear.

Values of the initial (steady-state) radical concentrations, C_0, were determined by comparison of the integrated intensity of the esr spectrum of the recombining radical with that of a known concentration of the stable di-*t*-butyl nitroxide radical. (The concentration of this standard was measured spectrophotometrically).[9] The standard sample was placed in the 400 Hz channel of the dual cavity and its spectrum was recorded simultaneously with that of tri-*t*-butylcycloheptatrienyl. Intensities were compared in terms of the product of the peak heights and the square of the line widths of the central components of the first-derivative spectra. An approximate study of the line shapes for the nitroxide and tri-*t*-butylcycloheptatrienyl radicals revealed that these are the same within experimental scatter[9b] and so a line shape factor does not enter into the intensity measurement.

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(1) Supported by the U. S. Army Research Office, Durham.

(2) Alfred P. Sloan Research Fellow.

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(4) (a) G. Porter and M. W. Windsor, *Nature*, **180**, 187 (1957); (b) R. L. McCarthy and A. MacLachlan, *Trans. Faraday Soc.*, **56**, 1187 (1960); (c) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964); (d) R. D. Burkhart, *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(5) Two closely related esr investigations are (1) a study of cyanoalkyl radical recombination (S. Weiner and G. S. Hammond, *ibid.*, **90**, 1659 (1968)) and (2) a study involving a pseudo second-order decay of CH_3-(aq) (D. Mickewich and J. Turkevich, *J. Phys. Chem.*, **72**, 2703 (1968)).

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(8) The full-scale pen-response time for this recorder is 0.3 sec. The response time of the esr spectrometer was never larger than one-tenth of the first half-life of the decaying signal.

(9) (a) A. K. Hoffman and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961); (b) for further details see M. L. Morrell, Ph.D. Thesis, University of Washington, Seattle, Wash., 1967.

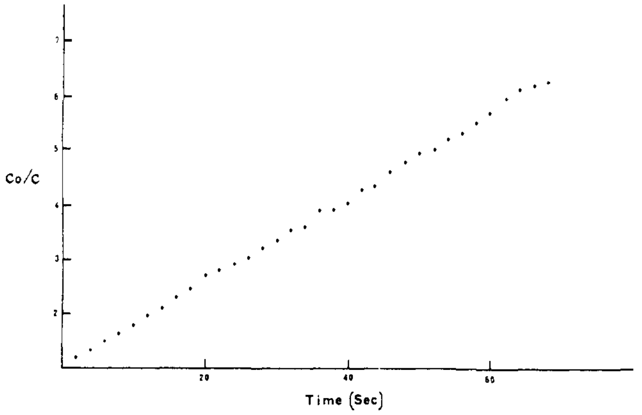

Figure 1. Plot of C_0/C *vs.* time for a typical run at −104° with a sample of dimer concentration 1.5×10^{-3} *M*.

Estimated maximum limits of error for C_0 and the absolute magnitude of k_{-1} are a factor of 2, and ±25% for relative values of k_{-1}. Rate constants are reproducible within ±10%.

Results and Discussion

The rate of decay of the esr signal of tri-*t*-butylcycloheptatrienyl radical in *n*-pentane has been measured as a function of temperature and concentration of dimer. Results of these measurements are presented in Table I.

Table I. Rate Constants and Activation Energies for the Recombination of Tri-*t*-butylcycloheptatrienyl Radicals

Dimer concn, *M*	Temp, °C	k_{-1},[a,b] M^{-1} sec^{-1}	ΔE_a, kcal/mol	No. of runs
0.4×10^{-3}	−107	2.9×10^4		3
1.5×10^{-3}	−104	2.6×10^4		3
	−46	1.7×10^5	1.9	3
	+18	2.8×10^5		3
6×10^{-3}	−106	3.0×10^4		5
	+22	2.3×10^5	1.6	3
8×10^{-2}	−112	4.2×10^4		3
(sample 1)	−86	1.1×10^5		3
	−49	1.8×10^5	1.4	3
	+22	3.5×10^5		4
8×10^{-2}	−111	3.5×10^4		4
(sample 2)	−90	9.3×10^4	1.8	5
	+22	4.3×10^5		3

[a] Rate constants were determined from each of the kinetic runs. The entries in this column are average values. [b] Values of the rate constants reported in this table and cited throughout this work are defined by the equation $-d[R\cdot]/dt = k_{-1}[R\cdot]^2$.

For all dimer concentrations less than 8×10^{-2} *M*, plots of C_0/C *vs.* time have been found to be linear over the measurable range of a factor of 6 or 7 in radical concentration. A typical plot is shown in Figure 1. This is excellent evidence that the decay process is second order and we therefore ascribe it to radical recombination. The results for the 8×10^{-2} *M* samples are discussed below.

The best data were obtained for the sample which was 1.5×10^{-3} *M* in dimer. This is so because (1) no underlying resonance[6,9b] was observed and (2) photochemical isomerization[6,9b] was negligible, as evidenced by a constancy of the esr spectral intensity over a 4–5 hr period. The first half-life varied from about 3 sec at 18° to about 10 sec at −104°. Corresponding recombination rate constants (k_{-1}) are *ca.* 3×10^5 and 3×10^4 M^{-1} sec^{-1}, respectively. A plot was made of ln k_{-1} *vs.* T^{-1} from which an Arrhenius activation energy, ΔE_a, of 1.9 ± 0.2 kcal/mol was obtained.[10]

The data for the 6×10^{-3} *M* sample yielded average rate constants at −106° and +22°. From these two values ΔE_a = 1.6 kcal/mol is computed.

For the 8×10^{-2} *M* samples, plots of C_0/C *vs.* time were linear for the first half-life and were also linear for *all* succeeding times but with a somewhat smaller slope. We have analyzed and reported the data for times following the first half-life. The activation energies obtained for the two samples are 1.4 and 1.8 kcal/mol. The average of the four determinations of activation energy is 1.7 kcal/mol (±0.3 kcal/mol total range of measurements).

A valuable internal check on the validity of our method is afforded by the good concordance among values of k_{-1} for similar temperatures and widely varying dimer concentrations.

A number of comments regarding our results can be made. (1) The recombination rate constant for tri-*t*-butylcycloheptatrienyl radical is considerably smaller than those of other hydrocarbon free radicals such as ethyl or benzyl, which are close to the diffusion-controlled values (see Table II).[11] This reduction is probably due principally to the steric effect of the three *t*-butyl groups, since the Arrhenius activation energy is only about 1.5–2.0 kcal/mol. (2) The activation energy is quite small and is thus comparable to that found for recombination of ethyl radicals in solution, namely 0.8 kcal/mol.[4c] Effects of electron delocalization and of steric compression in the transition state, which may account for the 8-kcal/mol activation energy in the case of triphenylmethyl radical,[3] are apparently not significant for tri-*t*-butylcycloheptatrienyl radical. (3) It is anticipated that the simple esr technique employed in this work[12] may find wide application in the determination of recombination rate constants for large π-electron radicals. Some possible examples are di- and triarylmethyls and xanthyl free radicals.[13]

Table II. Rate Constants for Recombination of Hydrocarbon Radicals in Liquid Solution

Radical	Solvent	Rate const, M^{-1} sec^{-1}	Temp, °C	Ref
Ethyl	Ethane	$(1.7 \pm 0.4) \times 10^8$	−177	4c
Pentyl	Benzene	$(2.0 \pm 0.6) \times 10^9$	25	4d
Benzyl	Benzene	$(8.2 \pm 2.4) \times 10^9$	25	4d
Benzyl	Ethanol + glycerol	6.5×10^8 [a]	*b*	4b
Benzyl	Paraffin	1.4×10^9 [a]	*c*	4a

[a] The extinction coefficient cited in ref 4d was employed. [b] Viscosity of 55 cP. [c] Viscosity of 163 cP.

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(10) As an approximate check we have also *estimated* the activation energy from the *relative* steady-state radical concentration as a function of temperature, $C_0(T)$. If the rate of photochemical production of radicals is assumed to be independent of temperature then one readily obtains the equation $[C_0(T_1)/C_0(T_2)]^2 = \exp[-(\Delta E/R)(1/T_2 - 1/T_1)]$. Using the relative concentrations for the 1.5×10^{-3} *M* sample an activation energy of 1.6 kcal/mol is computed which is in fairly good agreement with the value 1.9 ± 0.2 kcal/mol obtained from the temperature dependence of k_{-1}.

(11) A single experiment, of order-of-magnitude accuracy, was performed on the recombination of the unsubstituted cycloheptatrienyl radical, $C_7H_7\cdot$. The rate constant obtained is $2 \times 10^{+7}$ M^{-1} sec^{-1} +22°).

(12) See also W. J. McGuire and R. C. Pink, *Trans. Faraday Soc.*, **63**, 1098 (1967).

(13) M. D. Sevilla and G. Vincow, *J. Phys. Chem.*, **72**, 3635, 3641, 3647 (1968).