

Light Modulation-전자상자성공명법을 이용한 절대속도상수의 결정*

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The Absolute Rate Measurement by Light Modulation -ESR Technique*

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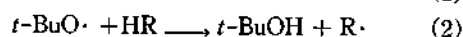
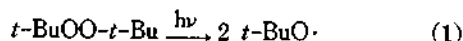
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요 약. Modulated light signal 과 trimethylsilyl 유리기의 전자상자성 공명 signal 과의 phase shift 를 측정함으로써 *t*-butoxy 유리기와 trimethylsilane 의 절대 반응속도 상수는 -50°C 에서 $3 \times 10^{-2} M^{-1} \cdot \text{sec}^{-1}$ 으로 얻을 수 있었다.

ABSTRACT. A rate constant is deduced for the reaction of *tert*-butoxy radicals and trimethylsilane from the measurement of the phase shift between the modulated light source and the ESR signal of trimethylsilyl radical. The rate constant was found to be $3 \times 10^{-2} M^{-1} \cdot \text{sec}^{-1}$ at -50°C .

INTRODUCTION

A time-resolved electron spin resonance spectroscopy has gained wide popularity as a technique for the study of free radical reactions in solution.^{1,2} The free radicals studied are generated *in situ* by photolysis or high energy irradiation with electrons or γ -rays. One of the most convenient precursors for the generation of free radicals in solution is di-tertiary-butyl peroxide which strongly absorbs radiation in the ultraviolet region.³



Decay of the secondary radical $\text{R}\cdot$ produced in reaction 2 and disappearing in reaction 3 can be studied directly by monitoring the electron spin resonance signal of $\text{R}\cdot$ in a brief time interval after its generation.²

Attempts to detect the electron spin resonance signal of the tertiary butoxy radical have thus far been unsuccessful. Weiner and Hammond reported the detection of *tert*- $\text{BuO}\cdot$ by esr spectroscopy during ultraviolet photolysis of pure *t*- $\text{BuOO-}t\text{-Bu}$.⁴ However the signal observed seems to have been due to *t*- $\text{Bu-O}_3\cdot$ rather

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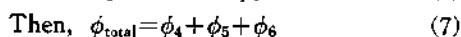
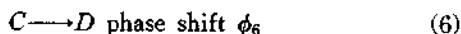
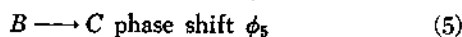
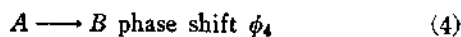
than $t\text{-Bu-O}\cdot$.⁵ In the presence of high concentrations of a hydrogen donor, the lifetime of $t\text{-BuO}\cdot$ may be too short for these radicals to be directly detected by esr spectroscopy if magnetic field modulation is employed in obtaining the spectra.

Relative rates of hydrogen abstraction by $t\text{-BuO}\cdot$ radicals from primary, secondary, and tertiary C—H bonds have been estimated.⁶ The rate of reaction of $t\text{-BuO}\cdot$ radicals with toluene leading to abstraction of a benzylic hydrogen atom has been reported.⁷ No absolute rate constant for hydrogen abstraction from Si—H bonds by $t\text{-BuO}\cdot$ radicals has been published, although this is known to be the most convenient for the generation of silicon-centered radicals.^{2,3}

In this paper we wish to report the absolute rate constant for hydrogen abstraction from trimethylsilane by $t\text{-BuO}\cdot$ radicals deduced from the measurement of the phase shift between the modulated light source employed in the photolysis of *tert*-butyl peroxide to $t\text{-BuO}\cdot$ radicals and the esr signal of trimethylsilyl radicals.

Application of light modulation, phase shift methods in chemical kinetics have been known for more than two decades.⁸⁻¹² These have been applied to the study of free radical chain reactions,⁹ quenching of fluorescence and energy transfer,⁸ absorption spectra of transient intermediates,¹⁰ decay of the triplet states,¹¹ and the reactions of atomic species.¹²

Light modulation, phase shift techniques not only provide another method for the measurement of the lifetimes of transient species which can be directly detected, but are unique in the ability to measure lifetimes of *undetected* species, if complete reaction mechanisms and other elementary reaction rates are known. The total phase shift in the reaction sequence is the sum of the phase shifts for each step:⁸



Therefore if one knows ϕ_4 and ϕ_6 and can experimentally observe ϕ_{total} , then one can deduce ϕ_5 from Eq. (7). This is the bases for our deduction of the rate constant for hydrogen abstraction from trimethylsilane by $t\text{-BuO}\cdot$, which has not been previously reported.

EXPERIMENTAL

General. A detailed description of the apparatus, the preparation of esr samples, the measurement of radical concentrations, and the general procedure for flash photolysis, electron spin resonance kinetic spectroscopy have been published elsewhere.² Trimethylsilane (Pierce Chemical Co.) was used without further purification, its purity having been established by gas chromatography and infrared spectroscopy. Di-*t*-butyl peroxide (Matheson, Coleman, and Bell) was purified by vacuum distillation at 90 torr. A middle fraction boiling at 52°C was taken.¹³ Reaction mixtures were 1:1 (V/V) mixtures of $(\text{CH}_3)_3\text{SiH}$ and $(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_3$. A 150 watt xenon flash lamp (Eimac R150-2) controlled by a variable on-off time pulse generator (Tectronix) was employed as the photolysis light source. The phase shift were measured by feeding the esr signal output from the esr spectrometer (Varian E-3) into the phase sensitive detector (PAR HR-8 lock-in amplifier) which was tuned to the pulse frequency (i.e. the output from the pulse generator) of the photolysis light source.

The total phase shift ϕ_{total} was determined from the relationship:¹²

$$\tan_{\text{total}} = \frac{\text{Intensity of the signal at } 90^\circ \text{ phase}}{\text{Intensity of the signal at } 0^\circ \text{ phase}} \frac{\text{relative to light}}{\text{relative to light}}$$

Therefore the ratios of the esr signal intensities at 0° and 90° phase angle relative to the light source give the observed phase shift of the directly observed esr signal at a given modulation frequency. Experimental data are displayed in Fig. 1.

Kinetic Analysis. The chemical reactions initiated by light in our system are:²

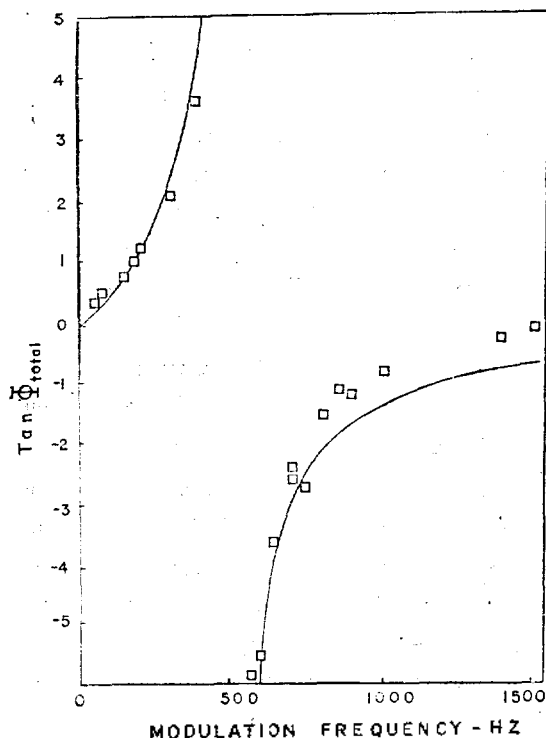
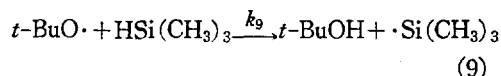
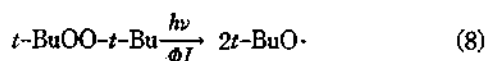
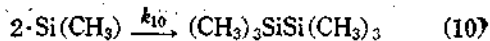


Fig. 1. Relationship between modulation frequency and phase shifts. Points indicated by \square were experimentally observed and the solid line was calculated from equation (17) with parameters shown in the text.



Φ is photolysis quantum yielded, I is the light intensity.

Photolysis is carried out by light pulses whose form approximates that of a square waves. The square wave function can be represented as a Fourier series of sine waves. If one selects (experimentally) the first harmonic of the series, the light intensity can be expressed as:

$$I = I_0/2 + I_0/2 \sin \omega t \quad (11)$$

I_0 is the maximum light intensity, $\omega = 2\pi\nu$ is the circular frequency of the modulation and ν is the repetition frequency in hertz.

It can be assumed that the phase shift due to the initial photolysis, reaction 8, is negligibly small. From reactions (8), (9) and (11) we may write:

$$\frac{d[t\text{-BuO}\cdot]}{dt} = \Phi I_0 + \Phi I_0 \sin \omega t - k_9 [t\text{-BuO}\cdot] [\text{HSi}(\text{CH}_3)_3] \quad (12)$$

It can readily be shown that integration yields a function of the form:

$$[t\text{-BuO}\cdot] = A \sin(\omega t - \phi_0) + B \quad (13)$$

A and B are time-independent functions of the concentration of $\text{HSi}(\text{CH}_3)_3$ which remains constant during an experiment.

$\phi_0 = \tan^{-1}(\omega/k_9[\text{HSi}(\text{CH}_3)_3])$, is the phase shift due to reaction (9).

From reactions (9) and (10) we obtain:

$$\frac{d[\cdot\text{Si}(\text{CH}_3)_3]}{dt} = k_9 [t\text{-BuO}\cdot] [\text{HSi}(\text{CH}_3)_3] - 2k_{10} [\cdot\text{Si}(\text{CH}_3)_3]^2 \quad (14)$$

Substitution of equation (13) into (14) gives:

$$\frac{d[\cdot\text{Si}(\text{CH}_3)_3]}{dt} = C \sin(\omega t - \phi_0) - 2k_{10} [\cdot\text{Si}(\text{CH}_3)_3]^2 + D \quad (16)$$

C and D are time-independent functions of the concentration of $\text{HSi}(\text{CH}_3)_3$, which remains constant during an experiment.

It can be shown that integration yields a function of the form:

$$[\cdot\text{Si}(\text{CH}_3)_3] = E \sin(\omega t - \phi_9 - \phi_{10}) + F \quad (16)$$

E is a time-independent function of $[\text{HSi}(\text{CH}_3)_3]$ and ω , both remaining constant during a given set of experiment. F is a time-independent function of $[\text{HSi}(\text{CH}_3)_3]$. $\phi_{10} = \tan^{-1}\{\omega/2(2k_{10}\phi I_0)^{1/2}\}$, is the phase shift due to reaction (10).

At moderately high modulation frequencies, such that $I = I_0$ and $d[\cdot\text{Si}(\text{CH}_3)_3]/dt = 0$, the total phase shift due to reactions (8) to (10), $\phi_{\text{total}} = \phi_9 + \phi_{10}$ can be obtained from the expression,

$$\begin{aligned} \tan \phi_{\text{total}} &= \tan(\phi_9 + \phi_{10}) = \\ &= \frac{K\omega / \{2k_9[\text{HSi}(\text{CH}_3)_3](2k_{10}\phi I_0)^{1/2} - \omega^2\}}{K = \{k_9[\text{HSi}(\text{CH}_3)_3] + 2(2k_{10}\phi I_0)^{1/2}\}} \end{aligned} \quad (17)$$

At high modulation frequencies $\omega^2 \gg 2k_9[\text{HSi}(\text{CH}_3)_3](2k_{10}\phi I_0)^{1/2}$ and Eq. (17) reduces to:

$$-K = \omega \tan \phi_{\text{total}} \quad (18)$$

Thus K can be obtained from experimentally determined total phase shifts, ϕ_{total} , at known values of the modulation frequencies. The experimentally observed relationship between total phase shifts and modulation frequencies is displayed in Fig. 2.

The desired rate constant k_9 was obtained from the intercept of a plot, presented in Fig. 2 of K versus $(\phi I_0)^{1/2}$. I_0 was varied with screens of known transmittance positioned between the photolysis flash lamp and the reaction mixture in the esr spectrometer cavity.² For each light intensity employed, $(\phi I_0)^{1/2}$ was obtained from the expression for the steady state radical concentration

$$[\cdot\text{Si}(\text{CH}_3)_3] = (\phi I_0 / 2k_{10})^{1/2} \quad (19)$$

employing the previously determined² value for $k_{10} = 0.9 \times 10^9 \text{ M}^{-1} \text{ sec}$ at -50°C .

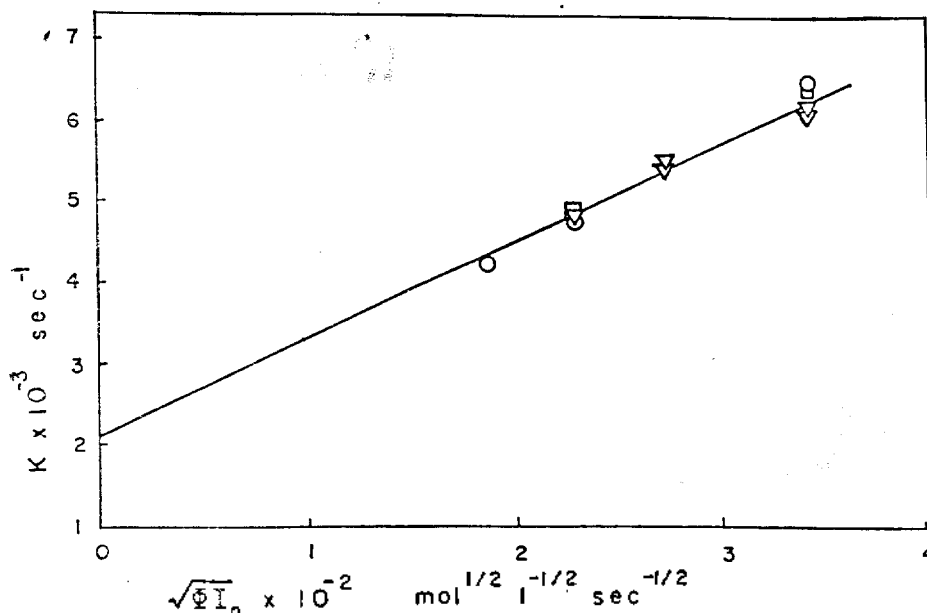


Fig. 2. Plot of K versus $(\phi I_0)^{1/2}$ (○: $\nu = 800 \text{ Hz}$, □: $\nu = 1100 \text{ Hz}$, △: $\nu = 1200 \text{ Hz}$).

RESULTS AND DISCUSSION

All phase shift measurements were carried out by monitoring the high field line of relative intensity 120 in the group of ten peaks whose relative intensities are 1:9:36:84:126:84:36:9:1. Typical esr signal intensities at different modulation frequencies and two different phases (A, in phase, 0° from light; B, out of phase, 90° from light) are shown in Fig. 3. As expected, the esr signal is not shifted in phase from the photolysis light source for very low modulation frequencies (e. g. 20cps, Fig. 3a). The phase shift of the esr signal from the light source increases with increasing modulation frequency (e. g. Fig. 3b~d).

The 130° phase shift of Fig. 3d indicates a mechanism in which more than one step contributes to the total phase shift. A single-step mechanism can lead to a maximum phase shift of 90° .⁸ For the two step mechanism suggested

here, the maximum phase shift is 180° . All data were taken at -50°C at which the esr signal-to noise ratio was found to be maximum.

Fig. 2 and Table 1 shows the plot of K versus $(\phi I_0)^{1/2}$, the latter quantity obtained from measurements of $\text{Si}(\text{CH}_3)_3$ radical concentrations and the rate constant for $\text{Si}(\text{CH}_3)_3$ dimerization as previously determined². From the intercept of Fig. 2 and the concentration of $\text{HSi}(\text{CH}_3)_3$ ($7M$) the rate constant for reaction 9, the abstraction of a hydrogen atom by the *t*-BuO radical from the Si-H bond of trimethylsilane is calculated to be $k_9 = 3 \times 10^2 M^{-1} \text{sec}^{-1}$ at -50°C .

The relationship between the total phase shift and modulation frequencies is shown in Fig. 1. and Table 2. The square point are experimental values while the solid line is calculated from Eq. (17) using values: $2k_{10} = 2 \times 10^9 M^{-1} \text{sec}^{-1}$,² $k_9[\text{HSi}(\text{CH}_3)_3] = 2.1 \times 10^3 \text{sec}^{-1}$ and $(\phi I_0)^{1/2} = 3.5 \times 10^{-2} M^2 \text{sec}^{1/2}$. A good agreement between experimental and calculation values

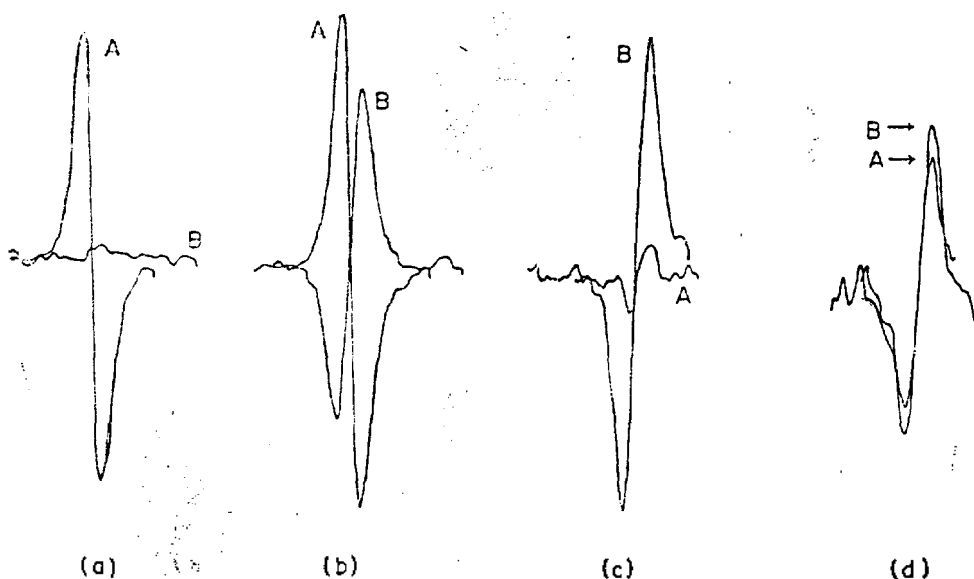


Fig. 3. Dependence on phase and modulation frequency of the esr signal intensity for the $\text{Si}(\text{CH}_3)_3$ radical. A is the signal at 0° phase angle relative to the flash lamp, B is the signal intensity at 90° phase angle relative to the flash lamp.

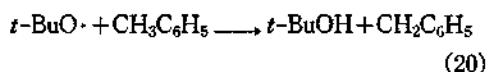
a. $\nu = 20 \text{ Hz}$, $\tan \phi_{\text{total}} = 0$, $\phi_{\text{total}} = 0^\circ$; b. $\nu = 150 \text{ Hz}$, $\tan \phi_{\text{total}} = 0.67$, $\phi_{\text{total}} = 34^\circ$; c. $\nu = 550 \text{ Hz}$, $\tan \phi_{\text{total}} = -7.4$, $\phi_{\text{total}} = 97^\circ$; d. $\nu = 850 \text{ Hz}$, $\tan \phi_{\text{total}} = -1.2$, $\phi_{\text{total}} = 130^\circ$.

Table 1. K (from equation 18) vs. $(\phi I_0)^{1/2}$ at different modulation frequencies.

Modulation Frequency (cps)	$K \times 10^{-3} (\text{sec}^{-1})$	$(\phi I_0)^{1/2} \times 10^2 (\text{mol}^{1/2} I^{-1/2} \text{sec}^{-1/2})$
800	6.52	2.30
	3.46	4.27
	4.66	1.86
1200	6.17, 6.23	3.46
	5.51, 5.46	2.77
	4.93, 4.75	2.30
1100	6.46	3.46
	5.50	2.77
	4.84	2.30

indicates the general validity of the kinetic analysis employed to interpret out ear phase shifts.

Ingold and coworkers have obtained the rate constant for the reaction



as $k_{20} = (8.0 \times 10^7) \exp(-5,600/RT) M^{-1} \text{sec}^{-1}$.¹⁴ At -50°C this corresponds to a rate constant $k_{20} = 3 \times 10^2 M^{-1} \text{sec}^{-1}$, which is very similar to k_9 obtained above.

It should be noted that this is the first application of a phase shift method to the determin-

Table 2. Modulation frequencies vs. phase shifts ($\tan\phi$).

Modulation frequency (CPS)	15	30	50	150	190	200	300	400	500	600	650	700	750	800	850	870	1000	1400	1500
$\tan\phi$	0	0.3	0.5	0.8	0.9	1.1	2.2	3.5	-19	-5.6	-3.7	-2.3	-2.7	-1.5	-1.0	-1.1	-0.88	-0.2	-0.1

ation by esr spectroscopy of a rate constant for a free radical whose esr signal could not be observed.

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