e_{aq}^-, H and OH Radicals in Aqueous Solution, NSRDS-NBS 70, Washington, 1988.
8. A. B. Ross and P. Neta, *Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solution*, NSRDS-NBS 70, Washington, 1982.
9. B. G. Ershov, E. Janata, and A. Henglein, *J. Phys. Chem.*, 1993, **97**, 4589.
10. B. G. Ershov, G. V. Ionova, and A. D. Kiseleva, *Zh. Fiz. Khim.*, 1994, **68**, 820 [*Russ. J. Phys. Chem.*, 1994, **68** (Engl. Transl.)].
11. B. G. Ershov and A. Henglein, *J. Phys. Chem.*, 1993, **97**, 3434.

Received February 12, 1999

Addition of carbon-centered radicals to C_{60}. Determination of the rate constants by the spin trap method

R. G. Gasanov, O. G. Kalina, V. V. Bashilov, and B. L. Tumanskii*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: tuman@ineos.ac.ru

The rate constants of addition of the $^{\cdot}\mathrm{CMe}_3$, $^{\cdot}\mathrm{CH_2Me}$, $^{\cdot}\mathrm{CH_2(CH_2)_3Me}$, $^{\cdot}\mathrm{CH_2Ph}$, $^{\cdot}\mathrm{CH_2CH{=}CH_2}$, and $^{\cdot}\mathrm{CH(Me)Et}$ radicals to fullerene C_{60} were determined by the method of competitive addition of free radicals to spin traps.

Key words: ESR, fullerene, radicals, spin traps, addition rate constants.

It is known that fullerenes can add various free radicals,[1–3] because of which they are called "radical sponges." Another feature of fullerenes is their high thermal stability, which allows them to be used in studying radical processes[4–5] occurring at 450—500 K, *e.g.*, as radical traps in studies of the kinetics of addition by the method of competitive reactions. Traditional radical traps, nitroso compounds, are unstable and decompose at temperatures ≥350 K. So far the specific use of fullerenes as radical traps has been limited for lack of data on the rate constants of addition of radicals to them. In the present work, the rate constants of addition of carbon-centered benzyl, allyl, and alkyl radicals to fullerene C_{60} were determined by ESR and the method of competitive reactions.[6]

Experimental

ESR spectra were recorded on a Varian E-12A spectrometer. Samples in glass tubes were degassed by several freezing—evacuating—thawing cycles and irradiated through UFS-2 and KS-15 filters with focused light produced by a DRSh-1000 lamp. Radicals $\mathrm{R}^1 = {}^{\cdot}\mathrm{CMe}_3$ were generated by photochemical decomposition (λ = 620—680 nm) of $\mathrm{Me_3CNO}$ and by elimination of Br atoms from $\mathrm{Me_3CBr}$ with $^{\cdot}\mathrm{Re(CO)_5}$ radicals,[7] which, in turn, have been obtained by photolysis of $\mathrm{Re_2(CO)_{10}}$ under the action of monochromatic UV radiation ($\lambda \approx 366$ nm):

$$\mathrm{Re_2(CO)_{10}} \xrightarrow{h\nu} 2\,{}^{\cdot}\mathrm{Re(CO)_5},$$

$$^{\cdot}\mathrm{Re(CO)_5} + \mathrm{BrCMe_3} \longrightarrow {}^{\cdot}\mathrm{CMe_3} + \mathrm{BrRe(CO)_5}.$$

By analogy, R^2—R^6 radicals were generated by elimination of Br or I atoms with rhenium-centered radicals: $\mathrm{R}^2 = {}^{\cdot}\mathrm{CH_2Me}$, $\mathrm{R}^3 = {}^{\cdot}\mathrm{CH_2(CH_2)_3Me}$, $\mathrm{R}^4 = {}^{\cdot}\mathrm{CH_2Ph}$, $\mathrm{R}^5 = {}^{\cdot}\mathrm{CH_2CH{=}CH_2}$, and $\mathrm{R}^6 = {}^{\cdot}\mathrm{CH(Me)Et}$. The starting halides and toluene were distilled in an argon atmosphere immediately before use. Radical traps (Sigma) were employed. Time variation of the ESR signal intensities for spin adducts of generated radicals with the traps and C_{60} were least-squares processed in the linear segment (correlation coefficient $R \geq 0.95$).

Results and Discussion

The method of competitive reactions rests on a comparison between the addition rate of free radicals to compounds under study (in this work, to fullerene C_{60}, stage (1)) and to spin traps (**T**) (stage (2)), for which the rate constants of addition of a large number of carbon-centered radicals are known.[6]

$$\mathrm{C_{60}} + {}^{\cdot}\mathrm{R} \xrightarrow{k_1} {}^{\cdot}\mathrm{C_{60}R}, \tag{1}$$

$$\mathrm{R} = \mathrm{R}^1\text{—}\mathrm{R}^6.$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 12, pp. 2369—2372, December, 1999.

1066-5285/99/4812-2344 $22.00 © 2000 Kluwer Academic/Plenum Publishers

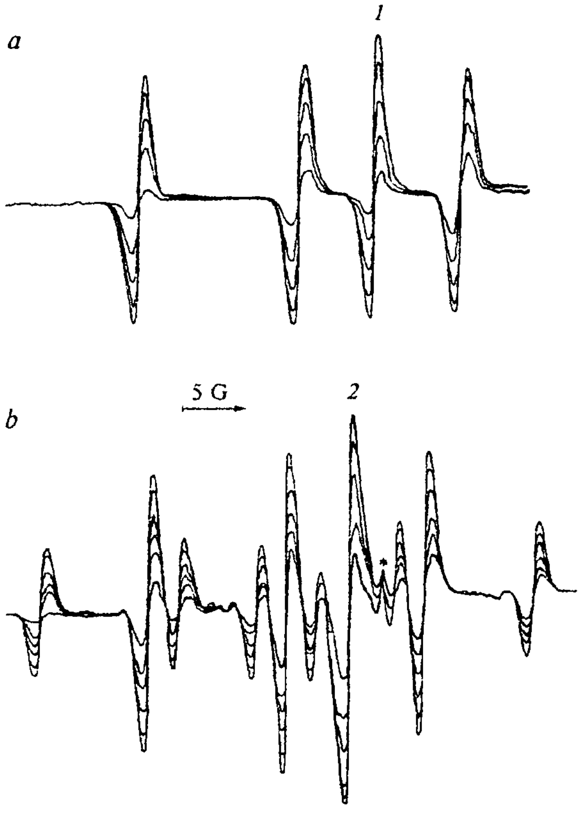


Fig. 1. ESR spectra of radical spin adducts obtained on irradiation of solutions in toluene with light with $\lambda \approx 366$ nm at 20 °C: (*a*) Me_3C with ND (t) and C_{60} (s, *1*). The starting solution contained Me_3CBr and $Re_2(CO)_{10}$; $[ND]_0 = 0.2653 \cdot 10^{-3}$ mol L^{-1}; $[C_{60}]_0 = 1.0 \cdot 10^{-3}$ mol L^{-1}; (*b*) Et with ND (tt) and C_{60} (s, *2*). The starting solution contained EtI and $Re_2(CO)_{10}$; $[ND]_0 = 0.5147 \cdot 10^{-3}$ mol L^{-1}; $[C_{60}]_0 = 1.0 \cdot 10^{-3}$ mol L^{-1}. A signal from quartz is asterisked.

Addition of $^{\cdot}R$ to **T** (nitroso compounds and α-phenyl-*N*-*tert*-butylnitron (PBN)) resulting in stable spin adducts ($^{\cdot}TR$) was used as a competitive reaction.

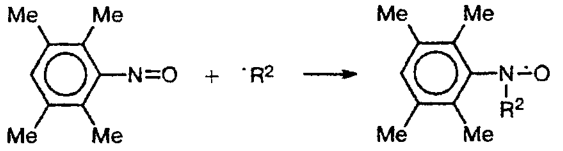
$$T + {}^{\cdot}R \xrightarrow{k_2} {}^{\cdot}TR \qquad (2)$$

The rate constants of addition of $^{\cdot}R$ to C_{60} were determined from

$$d[{}^{\cdot}TR]/d[{}^{\cdot}C_{60}R] = k_2[T]_0/k_1[C_{60}]_0,$$

where $[T]_0$ and $[C_{60}]_0$ are the initial concentrations of the spin trap and fullerene, respectively.

The concentrations of both $^{\cdot}TR$ and $^{\cdot}C_{60}R$ ($R = R^2$) increased simultaneously upon irradiation of solutions of C_{60}, BrR, and $Re_2(CO)_{10}$ in toluene containing a spin trap such as 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene, ND), the formation of spin adducts of $^{\cdot}Re(CO)_5$ with C_{60} escaping detection by ESR[8] (Fig. 1).



$$C_{60} + {}^{\cdot}R^2 \longrightarrow {}^{\cdot}C_{60}R^2$$

Similar regularities were observed when R^1 and R^3—R^6 radicals were used.

After irradiation is stopped, the ESR signal from the fullerenyl radical $^{\cdot}C_{60}R$ significantly decreases in the linear segment of the dependence of the signal intensity on time for a few seconds. Apparently, the fullerenyl radicals formed under these reaction conditions dimerize.

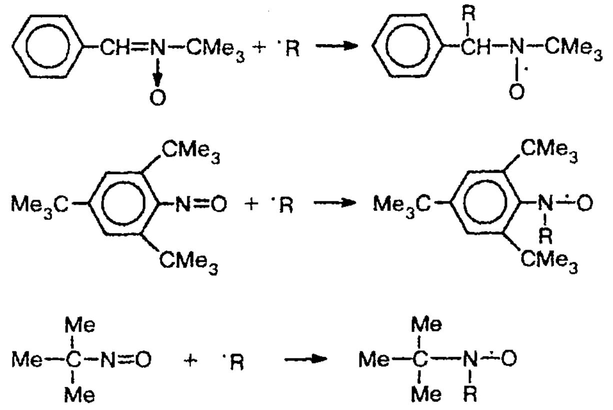
Table 1. Rate constants of addition of radicals $^{\cdot}R$ to fullerene ($[C_{60}] = 10^{-3}$ mol L^{-1}) at –20 °C

Run	$\dfrac{d[{}^{\cdot}TR]^*}{d[{}^{\cdot}C_{60}R]}$	$^{\cdot}R$	T	$[T]_0 \cdot 10^3$ /mol L^{-1}	k_1	k_2
					10^5 L mol^{-1} s^{-1}	
1	1.903	$^{\cdot}CMe_3$ (R^1)	MNP	15.32	266	33
2	9.130	$^{\cdot}CMe_3$ (R^1)	ND**	0.7959	174	2000
3	3.545	$^{\cdot}CMe_3$ (R^1)	ND	0.3316	187	2000
4	3.847	$^{\cdot}CH_2Me$ (R^2)	ND	0.5447	57	400
5	2.958	$^{\cdot}CH_2Me$ (R^2)	PBN	109.55	49	1.33
6	2.981	$^{\cdot}CH_2(CH_2)_3Me$ (R^3)	PBN	109.55	49	1.33
7	4.661	$^{\cdot}CH_2(CH_2)_3Me$ (R^3)	ND	0.4766	41	400
8	2.879	$^{\cdot}CH(Me)Et$ (R^6)	ND	0.3585	50	400
9	12.241	$^{\cdot}CH(Me)Et$ (R^6)	MNP	9.195	46	61
10	15.464	$^{\cdot}CH_2CH{=}CH_2$ (R^5)	ND	0.268	6.9	400
11	5.370	$^{\cdot}CH_2CH{=}CH_2$ (R^5)	BHB	6.867	6.0	4.7
12	3.923	$^{\cdot}CH_2Ph$ (R^4)	ND	0.187	2.7	57

* With consideration of HFS of the ESR spectrum and the width of signals from $^{\cdot}TR$ and $^{\cdot}C_{60}R$.

** Monomeric form of ND.

The reliability of the measured rate constants of addition of $^{\cdot}$R radicals to fullerene is confirmed by similar runs using other traps: PBN, 2,4,6-tri-*tert*-butylnitrosobenzene (BNB), and 2-methyl-2-nitrosopropane (MNP) (Table 1).



In the latter case, the trap itself serves as a source of a *tert*-butyl radical on irradiation with light with $\lambda \approx$ 620 nm because of cleavage of the C—N bond.

As can be seen in Table 1, the rate constants of addition of $^{\cdot}$R radicals to C_{60}, obtained with different spin traps, are not scattered widely (except for R = CMe_3, whose constants k_2 differ from each other by a factor of two[6]). Their values are two orders of magnitude higher than those for addition of radicals to a wide class of monosubstituted unsaturated compounds.[9,10] Such a high reactivity of C_{60} with respect to carbon-centered radicals (as compared to monosubstituted alkenes) is largely due to the presence of 30 double bonds in the molecule of C_{60} and some energy gain because of delocalization of an unpaired electron in the fullerenyl radical.[3] A decrease in the rate constants of addition of R^1—R^6 radicals to fullerene in this series is caused by a decrease in the reactivity of the radicals. Similar changes (occurring in agreement with each other) in the rate constants have also been observed in the addition of these radicals to spin traps (*cf.* runs *2*, *3*, *4*, *6*, and *8*) and to monosubstituted unsaturated compounds.[9,10]

Our rate constants of addition of free radicals to fullerenes allow using the latter more widely as spin traps, revealing differences in the reactivities of various fullerenes and their derivatives.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-32216a), the State Scientific and Technical Program "Current Trends in the Physics of Condensed Media" (Subprogram "Fullerenes and Atomic Clusters"), and the Scientific Training Center of Organometallic Chemistry (Project No. 234 of the Federal Target Program "Integratsiya").

References

1. P. J. Krusic, E. Wasserman, B. A. Parkinson, B. Malone, E. R. Holler, Jr., P. N. Keizer, J. R. Morton, and K. F. Preston, *J. Am. Chem. Soc.*, 1991, **113**, 6274.
2. J. R. Morton, F. Negri, and K. F. Preston, *J. Magnetic Resonance in Chemistry*, 1995, **33**, S20.
3. B. L. Tumanskii, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2396 [*Russ. Chem. Bull.*, 1996, **45**, 2267 (Engl. Transl.)].
4. P. J. Fagan, P. J. Krusic, C. N. McEwen, J. Lazar, D. H. Parker, N. Herron, and E. Wasserman, *Science*, 1993, **262**, 404.
5. B. L. Tumanskii, E. N. Shaposhnikova, V. V. Bashilov, S. P. Solodovnikov, N. N. Bubnov, and S. R. Sterlin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1222 [*Russ. Chem. Bull.*, 1997, **46**, 1174 (Engl. Transl.)].
6. R. G. Gasanov and R. Kh. Freidlina, *Usp. Khim.*, 1987, **56**, 447 [*Russ. Chem. Rev.*, 1987, **56**, 264 (Engl. Transl.)].
7. R. G. Gasanov, E. G. Sadykhov, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1031 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 936 (Engl. Transl.)].
8. S. Zhang, T. L. Brown, Y. Du, and J. R. Shapley, *J. Am. Chem. Soc.*, 1993, **115**, 6705.
9. *Substituent Effects in Radical Chemistry*, NATO ASIN, Series C, Reidel, Dordrecht, 1986, **189**, 123.
10. R. G. Gasanov, T. D. Churkina, L. V. Il'inskaya, K. A. Kochetkov, and D. E. Bodrov, *Dokl. Akad. Nauk*, 1992, **326**, 126 [*Dokl. Chem.*, 1992 (Engl. Transl.)].

Received March 1, 1999