

# **Table D – Inorganic and Organic Solutes in Nonaqueous Solutions**

A record of inorganic and organic solute reactions with Mu in solvents other than water

The data presented refers to ambient temperatures (293-298K) and normal pressure unless otherwise specified.

Code	Ion	Reaction	Type of Reaction	$k_M$ (in $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ )	Notes about measurement	Reference	$k_H$ (in $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ )	Notes about measurement	Reference	KIE = $k_M / k_H$
D1	Iodine ( $\text{I}_2$ ) in n-hexane	$\text{I}_2 + \text{Mu} \rightarrow \text{MuI} + \text{I}$ (possibly $\mu^+ + \text{I}_2^-$ )	probably abstraction but possibly reduction – electron transfer	$(2.9 \pm 1.0) \times 10^{11}$	N/A	Jean, Y.C., Ng, B.W., Ito, Y., Nguyen, T.Q. and Walker, D.C. <i>Hyperfine Interact.</i> , 1981, <b>8</b> , 351.	N/A			
D2	Iodine ( $\text{I}_2$ ) in n-heptane	$\text{I}_2 + \text{Mu} \rightarrow \text{MuI} + \text{I}$ (possibly $\mu^+ + \text{I}_2^-$ )	probably abstraction but possibly reduction – electron transfer	$(5.7 \pm 2.2) \times 10^{11}$	N/A	Stadlbauer, J.M., Venkateswaran, K., Porter, G.B. and Walker, D.C. <i>J. Phys. Chem.</i> , 1997, <b>101</b> , 4741.				
D3	Iodine ( $\text{I}_2$ ) in methanol	$\text{I}_2 + \text{Mu} \rightarrow \text{MuI} + \text{I}$ (possibly $\mu^+ + \text{I}_2^-$ )	probably abstraction but possibly reduction – electron transfer	$(7.0 \pm 1.2) \times 10^{10}$	N/A	Stadlbauer, J.M., Venkateswaran, K., Porter, G.B. and Walker, D.C. <i>J. Phys. Chem.</i> , 1997, <b>101</b> , 4741.				
D4	Nitrate ion $\text{NO}_3^-$ in methanol	$\text{NO}_3^- + \text{Mu} \rightarrow \text{N(OMu)O}_2^-$ (?)	combination	$(1.1 \pm 0.3) \times 10^9$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003 (in press)				
D5	Nitrite ion $\text{NO}_2^-$ in methanol	$\text{NO}_2^- + \text{Mu} \rightarrow \text{MuNO}_2^-$ (?)	combination	$(5.3 \pm 1.5) \times 10^9$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003 (in press)				
D6	Acetone in n-heptane	$(\text{CH}_3)_2\text{C}=\text{O} + \text{Mu} \rightarrow (\text{CH}_3)_2\text{C(OMu)}$	addition to carbonyl C=O bond with Mu attached to O atom (by analogy to reaction of Mu in aqueous solution)	$(1.05 \pm 0.2) \times 10^9$	N/A	Stadlbauer, J.M., Venkateswaran, K. and Walker, D.C. <i>Can. J. Chem.</i> , 1997, <b>75</b> , 74.				
D7	Aniline in n-hexane	$\text{C}_6\text{H}_5\text{NH}_2 + \text{Mu} \rightarrow \text{MuC}_6\text{H}_5\text{NH}_2$	addition into benzene ring	$(6.7 \pm 0.8) \times 10^9$	N/A	Louwrier, P.W.F., Brinkman, G.A. and Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 831.				
D8	Benzene - neat	$\text{C}_6\text{H}_6 + \text{Mu} \rightarrow \text{MuC}_6\text{H}_6$	addition into benzene ring	$(8.9 \pm 0.6) \times 10^9$ <i>(deduced indirectly)</i>	N/A	Roduner, E. <i>Hyperfine Interact.</i> , 1984, <b>17-19</b> , 785.				

D9	Benzene in n-hexane	$C_6H_6 + Mu \rightarrow MuC_6H_6$	addition into benzene ring	$(3.7 \pm 0.08) \times 10^9$	$E_a = (2 \pm 2) \text{ kJ mol}^{-1}$	Louwrier, P.W.F., Brinkman, G.A. and Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 831.
D10	Benzene in isopentane	$C_6H_6 + Mu \rightarrow MuC_6H_6$	addition into benzene ring	$4.51 \times 10^9$	$E_a = (6.0 \pm 1.0) \text{ kJ mol}^{-1}$ for T = 136.4 K to 295.0 K	Ganti, R. and Jean, Y.C. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 819.
D11	Benzene in methanol	$C_6H_6 + Mu \rightarrow MuC_6H_6$	addition into benzene ring	$(8.51 \pm 1.3) \times 10^9$	N/A	Louwrier, P.W.F., Brinkman, G.A. and Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 831.
D12	Carbon tetrachloride in methanol	$CCl_4 + Mu \rightarrow MuCl + CCl_3$	most likely abstraction	$\approx 5 \times 10^8$	N/A	Roduner, E. <i>Hyperfine Interact.</i> , 1984, <b>17-19</b> , 785.
D13	1,4-Difluorobenzene in n-hexane	$p-C_6H_4F_2 + Mu \rightarrow p-C_6H_4F_2Mu$	addition into benzene ring	$(2.5 \pm 0.5) \times 10^9$	N/A	Louwrier, P.W.F., Brinkman, G.A. and Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 831.
D14	2,3-Dimethylbutadiene-1,3 (DMBD) in n-hexane	$CH_2 = C(CH_3)-(CH_3)C=CH_2 + Mu \rightarrow MuCH_2(CH_3)-(CH_3)C=CH_2$	addition across C=C bond (formation of 1,1,2-trimethyl allyl radical)	$(1.4 \pm 0.2) \times 10^{11}$	T = 288 K  $E_a = (6.5 \pm 1.7) \text{ kJ mol}^{-1}$ for T = 185 K to 333 K	Roduner, E., Louwrier, P.W.F., Brinkman, G.A., Garner, D.M., Reid, D., Arseneau, D.J., Senba, M. and Fleming, D.G. Ber. Bunsenges. Phys. Chem., 1990, 94, 1224.
D15	2,3-Dimethylbutadiene-1,3 in acetone	$CH_2 = C(CH_3)-(CH_3)C=CH_2 + Mu \rightarrow MuCH_2-C(CH_3)-(CH_3)C=CH_2$	addition across C=C bond (formation of 1,1,2-trimethyl allyl radical)	$(9.1 \pm 1.9) \times 10^{10}$ <i>(deduced indirectly)</i>	N/A	Roduner, E. <i>Radiat. Phys. Chem.</i> , 1986, <b>28</b> , 75
D16	2,3-Dimethylbutadiene-1,3 (DMBD) in methanol	$CH_2 = C(CH_3)-(CH_3)C=CH_2 + Mu \rightarrow MuCH_2C(CH_3)-(CH_3)C=CH_2$	addition across C=C bond (formation of 1,1,2-trimethyl allyl radical)	$(7.4 \pm 0.1) \times 10^{10}$	T = 289 K	Roduner, E., Louwrier, P.W.F., Brinkman, G.A., Garner, D.M., Reid, D., Arseneau, D.J., Senba, M. and Fleming, D.G. Ber. Bunsenges. Phys. Chem., 1990, 94, 1224.

N/A

<b>D17</b>	2,3-Dimethylbutadiene-2,3 (DMBD) in n-octane	$\text{CH}_2 = \text{C}(\text{CH}_3) - (\text{CH}_3)\text{C} = \text{CH}_2 + \text{Mu} \rightarrow (\text{Mu})\text{CH}_2\text{C}(\text{CH}_3) - (\text{CH}_3)\text{C} = \text{CH}_2 + \text{Mu}$	addition across C=C bond (formation of 1,1,2-trimethyl allyl radical)	$(8.8 \pm 1.1) \times 10^{10}$	T = 294 K	Roduner, E., Louwrier, P.W.F., Brinkman, G.A., Garner, D.M., Reid, D., Arseneau, D.J., Senba, M. and Fleming, D.G. Ber. Bunsenges. Phys. Chem., 1990, 94, 1224.
<b>D18</b>	Dimethylsulfoxide (DMSO) - neat	$(\text{CH}_2)\text{SO} + \text{Mu} \rightarrow (\text{CH}_3)_2\text{SOMu}$	probably addition to S=O bond	$\approx 3 \times 10^8$ <i>(value estimated)</i>	N/A	Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 741.
<b>D19</b>	2,2,4,4-Tetramethyl-3-pentanone in n-heptane (di-tert-butyl ketone – DTBK)	$(\text{CH}_3)_3\text{C}(=\text{O})(\text{CH}_3)_3 + \text{Mu} \rightarrow (\text{CH}_3)_3\text{C}(\text{OMu})(\text{CH}_3)_3$	addition across C=O bond with Mu attached to O atom	$(6.6 \pm 1.5) \times 10^8$	N/A	Stadlbauer, J.M., Venkateswaran, K. and Walker, D.C. <i>Can. J. Chem.</i> , 1997, <b>75</b> , 74.
<b>D20</b>	TEMPO-2,2,6,6-tetramethyl-1-piperidinyloxy (free radical) in n-hexane	$\text{TEMPO} + \text{Mu} \rightarrow \text{TEMPO}(\text{Mu})$ $\text{TEMPO} + \text{Mu} (\uparrow\uparrow) \rightarrow \text{TEMPO} + \text{Mu}(\uparrow\downarrow)$	combination and spin (?) exchange	$(8.0 \pm 2.0) \times 10^{10}$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003, <b>81</b> , 175
<b>D21</b>	TEMPO-2,2,6,6-tetramethyl-1-piperidinyloxy (free radical) in n-methanol	$\text{TEMPO} + \text{Mu} \rightarrow \text{TEMPO}(\text{Mu})$ $\text{TEMPO} + \text{Mu} (\uparrow\uparrow) \rightarrow \text{TEMPO} + \text{Mu}(\uparrow\downarrow)$	combination and spin (?) exchange	$(4.8 \pm 0.7) \times 10^{10}$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003, <b>81</b> , 175
<b>D22</b>	TEMPO-OH 2,2,6,6-tetramethyl-4-hydroxy-1-piperidinyloxy (free radical) in n-hexane	$\text{TEMPO-OH} + \text{Mu} \rightarrow \text{OH-TEMPO-Mu}$ $\text{TEMPO-OH} + \text{Mu} (\uparrow\uparrow) \rightarrow \text{OH-TEMPO} + \text{Mu}(\uparrow\downarrow)$	combination and spin (?) exchange	$(6.0 \pm 2.0) \times 10^{10}$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003, <b>81</b> , 175

N/A

D23	TEMPO-OH-2,2,6,6-tetramethyl-4-hydroxy-1-piperidinyloxy (free radical) in n-methanol	TEMPO-OH + Mu → OH-TEMPO (Mu)  TEMPO-OH + Mu (↑↑) → TEMPO-OH + Mu(↑↓)	combination and spin (?) exchange	$(5.0 \pm 1.0) \times 10^{10}$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003, <b>81</b> , 175
D24	Ethylene in methane	$\text{CH}_2=\text{CH}_2 + \text{Mu} \rightarrow (\text{Mu})\text{CH}_2-\text{CH}_2$	addition across olefinic bond	$2.1 \times 10^{10}$	T = 110 K A = $1.9 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ E <sub>a</sub> = $(1.7 \pm 0.4) \text{ kJ mol}^{-1}$ for T = 83 K to 110 K	Jean, Y.C., Ganti, R.L., Cheng, K.L., Venkateswaran, K. and Walker, D.C. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 813.
D25	Ethylene in 2-methylbutane	$\text{CH}_2=\text{CH}_2 + \text{Mu} \rightarrow (\text{Mu})\text{CH}_2-\text{CH}_2$	addition across olefinic bond	$2.6 \times 10^{10}$	T = 295 K A = $1.5 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ E <sub>a</sub> = $(4.3 \pm 0.7) \text{ kJ mol}^{-1}$ for T = 133 K to 298 K	Jean, Y.C., Ganti, R.L., Cheng, K.L., Venkateswaran, K. and Walker, D.C. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 813.
D26	Hexafluorobenzene in n-hexane	$\text{C}_6\text{F}_6 + \text{Mu} \rightarrow \text{MuC}_6\text{F}_6$	addition into benzene ring	$(6 \pm 4) \times 10^7$	N/A	Louwrier, P.W.F., Brinkman, G.A. and Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 831.
D27	Naphthalene in n-hexane	$\text{C}_{10}\text{H}_8 + \text{Mu} \rightarrow \text{MuC}_{10}\text{H}_8$	addition	$(1.3 \pm 0.2) \times 10^{11}$	N/A	Jean, Y.C., Ng, B.W., Stadlbauer, J.M. and Walker, D.C. <i>J. Chem. Phys.</i> , 1981, <b>75</b> , 2879.
D28	Nitrobenzene in n-hexane	$\text{C}_6\text{H}_5\text{NO}_2 + \text{Mu} \rightarrow \text{MuC}_6\text{H}_5\text{NO}_2$	addition	$(1.3 \pm 0.15) \times 10^{10}$	N/A	Karolczak, S., Gillis, H.A., Porter, G.B. and Walker, D.C. <i>Can. J. Chem.</i> , 2003, <b>81</b> , 175
D29	Phenol in n-hexane	$\text{C}_6\text{H}_5\text{OH} + \text{Mu} \rightarrow \text{MuC}_6\text{H}_5\text{OH}$	addition into benzene ring	$(7 \pm 1.0) \times 10^9$	N/A	Ito, Y., Ng, B.W., Jean, Y.C. and Walker, D.C. <i>Can. J. Chem.</i> , 1980, <b>58</b> , 2395.
D30	Phenol in methanol	$\text{C}_6\text{H}_5\text{OH} + \text{Mu} \rightarrow \text{MuC}_6\text{H}_5\text{OH}$	addition into benzene ring	$(3.3 \pm 1.0) \times 10^{10}$	N/A	Jean, Y.C., Ng, B.W., Stadlbauer, J.M. and Walker, D.C. <i>J. Chem. Phys.</i> , 1981, <b>75</b> , 2879.

N/A

D31	2-Propanol in n-hexane	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{Mu} \rightarrow \text{CH}_3\text{C}(\text{OH})\text{CH}_3$	H-abstraction	$7 \times 10^6$	N/A	Venkateswaran, K., Barnabas, M.V., Wu, Z., Stadlbauer, J.M., Ng, B.W. and Walker, D.C. <i>Chem. Phys. Lett.</i> , 1988, <b>143</b> , 313.	N/A
D32	Styrene in n-hexane	$\text{C}_6\text{H}_5\text{-CH=CH}_2 + \text{Mu} \rightarrow \text{C}_6\text{H}_5\text{-CH-CH}_2 \text{ Mu}$	addition mainly to vinyl bond	$(6.0 \pm 0.6) \times 10^{10}$	N/A	Louwrier, P.W.F., Brinkman, G.A. and Roduner, E. <i>Hyperfine Interact.</i> , 1986, <b>32</b> , 831	