polymer communications

Semi-empirical calculation of probabilities of radical formation at various sites in a 2,6,10-trimethyl undecane

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(Received 6 April 1994; revised 11 August 1994)

Semi-empirical calculations were done on a 2,6,10-trimethyl undecane to determine the activation energy for radical formation at various carbon sites. The results obtained were compared with probability of radical formation determined experimentally.

(Keywords: semi-empirical calculation; activation energy; free radical reaction)

Introduction

In order to understand the mechanism of free radical graft reactions onto high molecular weight polyolefins, squalane and related small molecules have been the targets for quite sometime. Characterization of less than 5% grafted polyolefin materials is extremely difficult and has been one of the major reasons for the use of smaller molecules in mechanistic studies.

Recently, Kissin[1] has reported thermocracking of squalane, phytane and pristane at 250°C for 24 h and analysing by high resolution capillary gas chromatography. The relative population of radicals reported from such thermocracking of squalane is shown in *Figure 1*. Interestingly, the tertiary protons in the middle of the molecule could have a better radical population compared to those at the chain ends. Similarly, Russell and Kelusky[2] have reported successful mechanistic studies of grafting maleic anhydride onto polyolefins. Such grafting reactions and reaction mechanisms have been studied in an extruder by different groups[3,4].

We have been studying functionalization of polyolefins[5–8], hence our interest in mechanistic studies on squalane. Squalane can be envisioned as a model compound for ethylene–propylene copolymer. In this study we report our initial work on activation energy calculations on 2,6,10-trimethyl undecane, which has been used as a squalane prototype molecule, and compare our results with the relative radical population obtained by thermocracking experiments as reported by Kissin[1].

Semi-empirical calculations have been used to calculate activation energies of chemical reactions with considerable success[9]. We have used these calculations to predict the relative ease of radical formation and match them with the experimental results.

Calculation

We have used the semi-empirical package MOPAC 6.0 (purchased from Quantum Chemistry Program Exchange) to calculate the activation energies. AM1 Hamiltonian was used in all the calculations[10]. The structure of 2,6,10-trimethyl undecane is shown in *Figure 2*. It is similar to squalane. The symmetric half was omitted to limit the number of atoms to less than 50. For each of the atoms marked in *Figure 2*, the activation energy was obtained by calculating the reaction profile for C–H bond breaking. These were the atoms for which experimental data on relative population were available. A full geometry optimization was done for each structure; symmetry constraint was not used. All the calculations were done on an IBM 550/6000.

Results

The activation energies relative to carbon d(C-d), are shown in *Table 1*. The higher the relative activation energy the more difficult it is to form the radical. It can be seen from *Table 1* that the activation energy follows the same trend as the relative abundance. The only discrepancy between the calculated and experimental results is seen to be with the end carbon atoms. These atoms are in an unnatural environment and have

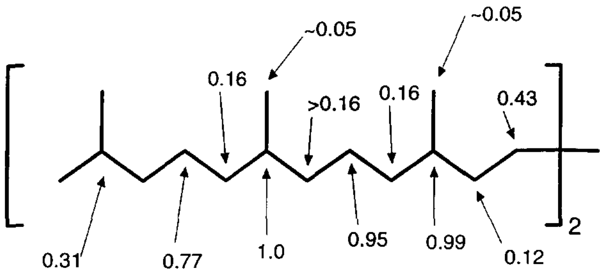

Figure 1 The relative population of radicals from thermocracking of squalane[1]

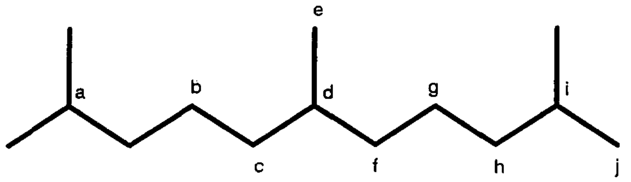

Figure 2 The numbering scheme for 2,6,10-trimethyl undecane used in the calculation

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0032-3861/94/24/5364–02

Table 1 Comparison of calculated activation energies with experimental relative radical abundance

Carbon no.	Relative activation energy (kcal mol^{-1})	Reported relative radical abundance[1]
a	−2.0	0.31
b	2.4	0.77
c	3.6	0.16
d	0.0	1.0
e	8.1	0.05
f	3.2	0.16
g	2.1	0.95
h	3.7	0.16
i	−1.0	0.99
j	7.5	0.05

considerable freedom of conformation compared with the situation in a melt. Carbon atoms C-g and C-i have activation energies of 2.1 and −1.0, respectively, with corresponding relative abundances of 0.95 and 0.99. The negative sign indicates that C-i is favoured in comparison to C-d to form the radical. Since the relative abundance for C-i is 0.99, we consider that there is no discrepancy between the calculated and experimental results. Atoms C-c, C-f and C-h, all of which have a relative abundance of 0.16, have activation energies in the range of 3.2–3.7. The carbon atoms with the least relative abundance, C-e and C-j, have the highest activation energy, 8.1 and 7.5, respectively. Thus the relative abundance of radical formation can be seen to be linked with the activation energy for the radical formation.

Conclusion

Semi-empirical calculations have successfully predicted the radical formation for 2,6,10-trimethyl undecane. (We thank the referees for pointing out the influence of tacticity on the results. The calculated molecule is isotactic, the experimental sample to our knowledge is a mixture. This might explain some of the minor differences observed between the calculated and experimental results.) The results compare well with experimental observations. Thus we can predict the probability of radical formation at a particular site. We have reported here the activation energies for the carbon atoms for which experimental data on relative abundance are available. Similar calculations can be applied to other systems and we are currently pursuing such calculations.

References

1 Kissin, Y. V. *Ind. Eng. Chem. Res.* 1987, **26**, 1633

2 Russell, K. E. and Kelusky, E. C. *J. Polym. Sci., Part A, Polym. Chem.* 1988, **26**, 2273

3 Ganzeveld, K. J. and Janssen, L. P. B. M. *Polym. Eng. Sci.* 1992, **32**, 467

4 Shing, J. B. W., Baker, W. E. and Russell, K. E. *Am. Chem. Soc., Polym. Prepr.* 1993, **34**, 364

5 Jois, Y. H. R., Harrison, J. B., Dery, M. E. and Pasternak, M. Paper presented at '2nd International Conference on Additives and Modifiers for Polymer Blends', 24–26 February 1993, Philadelphia, PA, USA

6 Jois, Y. H. R., Harrison, J. B., Hellmuth, K. and Flynn, D. J. Paper presented at 'Polymer Blends/Compatibilization', 1–2 June 1993, University of Connecticut, Storrs, CT, USA

7 Flynn, D. J. and Jois, Y. H. R. Technical Poster Session, American Chemical Society, 12 November 1993, Texaco Inc., Beacon, NY, USA

8 Jois, Y. H. R., Bronk, J. M., McCormack, A. J., Harrison, J. B., Drinkwater, D. E. and Sieber, J. R. Paper presented at Organic Division, 208th ACS National Meeting, 21–26 August 1994, Washington, DC, USA

9 Hehre, W. J., Burke, L. D., Shusterman, A. J. and Pietro, W. J. 'Experiments in Computational Organic Chemistry', Wavefunction Inc., Irvine, CA, USA, 1993

10 Dewar, M. J. S., Zoebisch, E. G., Healy, F. and Stewart, J. J. P. *J. Am. Chem. Soc.* 1985, **107**, 3902